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LEWIS MILLS NORTON.

THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

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VOLUME XV.

1893.

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COMMITTEE ON PAPERS AND PUBLICATIONS:

EDWARD HART, Editor,

J. H. LONG,

EDGAR F. SMITH.

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1. The first part of the document is a list of names and addresses of the members of the committee.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE COMPOSITION OF CERTAIN MODERN POWDERS.

BY CHARLES E. MUNROE.

THE powders examined belong principally to the class known in commerce as nitro-powders, and they are of interest since it is claimed for them that, when used as ballistic agents, they are more or less smokeless.

The method of analysis employed was as follows: The substance was first dried to constant weight over calcium chloride and the loss thus determined is noted as "volatile," though it was principally, when not wholly, hygroscopic moisture. A portion of the well-dried sample was then digested in ether-alcohol until disintegrated, the viscous solution formed was somewhat diluted and then poured upon an asbestos filter.

These filters were prepared by drawing out very light glass test tubes to a narrow funnel and chocking the neck with asbestos, which was exhausted with ether-alcohol and ether, and dried to constant weight. The filter with its charge was now suspended in a beaker partly filled with ether-alcohol so that the powder was immersed in the liquid, the whole covered so as to prevent loss by volatilization, and when the viscous fluid had passed through, the residue was washed with ether-alcohol until solution ceased. The residue was then dried to constant weight. This immersion was found necessary to prevent clogging by evaporation.

The ether-alcohol filtrate was treated with three volumes of chloroform to precipitate the soluble cellulose nitrates, which

(First reprint, March, 1894.)

were then collected on a filter, dried, and weighed. They appear in the tables under the technical name of "nitro-cotton." The filtrate from the ether-alcohol-chloroform solution was evaporated and the salts present determined. The residue insoluble in ether-alcohol was treated with boiling water so long as any solvent action continued. The residue then remaining was again dried and weighed. Finally it was exhausted with ethyl acetate and again dried and weighed. The loss by exhaustion with ethyl acetate is noted as "gun cotton" and the residue as cellulose. The metallic salts present were now determined in the aqueous solution.

When nitroglycerine was found to be present the dried powder was first exhausted with ether in a Soxhlet extractor and the loss noted as nitroglycerine, though as shown later it sometimes included resins or oil which were present in slight proportion.

When the powder was readily attacked by water, as was the case with the American Wood and Brackett Powders, the aqueous treatment preceded that by ether-alcohol, and the salts were thus extracted together with the product of the charring of the wood which is called "humus" in the tables. This "humus" was determined by evaporating the aqueous extract to constant weight on the water bath, then treating with nitric acid repeatedly until oxidation ceased, again evaporating to dryness, and then fusing gently.

To determine the aurin, which appears in several of the powders the sample was exhausted with chloroform in a Soxhlet extractor, and the residue in the tared flask weighed. The residue was then taken up with a few drops of chloroform, transferred to a separating funnel, shaken with strong ammonia water, and separated. The chloroform solution was repeatedly washed with dilute ammonia until no pink color was developed in the water, then the chloroform solution was again evaporated in the tared flask and the weight of the residue determined. The difference in the two weights is the aurin.

The results obtained were as follows:

*Schultze Gunpowder.*—The powder was marked "Improved Waterproof, New Issue," and was in the form of nearly spherical

grains which were almost white in color, though having a slight yellowish cast, and of such a size as to pass through a No. 20 mesh sieve. The results of the analysis on the specimen as received were as follows:

	Per cent.
Nitro-cotton.....	27.71
Gun cotton.....	32.66
Cellulose.....	1.63
Paraffin .....	4.20
Barium nitrate .....	27.62
Sodium nitrate .....	2.88
Potassium nitrate .....	2.47
Volatile .....	1.48
	<hr/>
	100.65

*E. C. Gunpowder.*—The package was marked E. C. Smokeless Sporting Powder, No. 1. "1 lb. of the powder is equivalent to 2 lbs. of the Best Black Powder. This powder does not absorb moisture from the atmosphere; but should it be accidentally wetted it may be again rendered fit for use by drying at a temperature not exceeding that of boiling water, and afterwards exposing it to the air for a day or more."

The grains were similar in size and shape to those of the Schultze powder described above, but they were orange colored. The composition was found to be:

	Per cent.
Nitro-cotton.....	53.57
Gun cotton.....	1.86
Cellulose.....	3.12
Barium nitrate .....	34.26
Sodium nitrate .....	3.67
Potassium nitrate .....	1.48
Aurin .....	0.55
Volatile .....	1.17
	<hr/>
	99.68

*American Wood Powder, Grade C.*—This powder was in rounded grains, of a dark brown color, and of such size as to pass through a No. 21 mesh. According to the accompanying circular Grade C "is for general use. Medium coarse. Good in any gun. Is strong, gives good pattern, and is the best all-



round powder made." The composition was found to be as follows:

	Per cent.
Soluble nitro-lignin .....	29.25
Insoluble nitro-lignin .....	14.06
Lignin (charred) .....	28.08
Humus .....	10.32
Sodium nitrate .....	15.27
Volatile .....	3.01
	<hr/>
	99.99

*American Wood Powder, Grade E.*—This powder resembled Grade C in form and color of grain, but passed through a No. 32 mesh. The accompanying circular stated that this grade is "Fine. The quickest of the lettered grades. For 16 to 20 bore guns, and rifles smaller than 45 calibres."

Analysis gave the following:

	Per cent.
Soluble nitro-lignin .....	24.91
Insoluble nitro-lignin .....	25.62
Lignin (charred) .....	19.15
Humus .....	8.65
Sodium nitrate .....	17.81
Volatile .....	3.86
	<hr/>
	100.00

*American Wood Powder. Ten Bore Trap.*—This powder had a brown color and was in rounded grains of such size as to pass through a No. 19 mesh. According to the circular this grade "is about of size of C. Is too quick for larger bores."

Analysis gave:

	Per cent.
Soluble nitro-lignin .....	33.21
Insoluble nitro-lignin .....	18.69
Lignin (charred) .....	20.27
Humus .....	10.65
Sodium nitrate .....	14.82
Volatile .....	2.36
	<hr/>
	100.00

*American Wood Powder—Twelve Bore Trap.*—This powder had a brown color and was in rounded grains of such size as to pass through a No. 24 mesh. The circular stated that "Twelve bore trap is very quick. In size about the same as D. It is too quick for 10 bores unless very small loads are used."

**Analysis gave:**

	Per cent.
Soluble nitro-lignin .....	29.47
Insoluble nitro-lignin.....	21.85
Lignin (charred) .....	16.59
Humus.....	15.62
Sodium nitrate .....	13.38
Volatile .....	3.14
	<hr/>
	100.05

*American Wood Powder.*—The foregoing samples were all purchased of D. Kirkwood, of Elm street, Boston, Mass. Another sample obtained from Martin and Company, of Newport without any mark, consisted of light brown rounded grains about the size of fuze powder, which were highly porous and quite friable.

**Analysis gave:**

	Per cent.
Soluble nitro-lignin.....	24.90
Insoluble nitro-lignin.....	30.07
Lignin (lightly charred).....	19.55
Humus.....	9.89
Sodium nitrate .....	9.76
Volatile .....	5.83
	<hr/>
	100.00

*Brackett's Sporting Powder.*—The sample of this powder which was also obtained from D. Kirkwood, Elm street, Boston, Mass., had the same general appearance as the American Wood Powders except that its grains were larger. About one-half of these grains passed through a twenty mesh sieve, while the remainder passed through a twelve mesh sieve. The circular stated that this powder was a strong quick powder intended for wing and bush shooting. Like the American Wood Powders the grains were porous and friable.

**Analysis gave:**

	Per cent.
Soluble nitro-lignin.....	31.43
Insoluble nitro-lignin.....	13.70
Lignin (charred) .....	13.22
Humus.....	18.94
Sodium nitrate.....	19.76
Volatile .....	2.93
	<hr/>
	99.98

*S. K. Powder.*—This package was marked "Smokeless (S.K.) Rook Rifle Gun Powder, made by the Smokeless Powder Company, Limited, at Barwick Works, Herts, England." The grains resembled those of the E. C. powder described above, except that the S. K. grains were more nearly lenticular and were pink colored. The granulation was such that the powder all passed through No. 24 sieve, and the granulation was quite uniform. The powder emitted a slight fragrant odor suggesting purified wood spirits.

Analysis gave :

	Per cent.
Nitro-cotton.....	20.39
Gun cotton.....	57.73
Aurin (alkaline).....	1.11
Barium nitrate .....	18.08
Potassium nitrate .....	1.24
Volatile.....	1.43
	<hr/>
	99.98

It will be noted that the coloring matter found, aurin, is the same as that found in the E. C. powder, yet the S. K. powder is colored pink or purple red while the E. C. was orange colored. As aurin (pararosaniline acid,  $C_{12}H_{11}O_3$ ) is orange colored when neutral, and pink to purple red when treated by alkalis, it is evident that the varying conditions of neutrality accounts for the difference in color.

The powder appeared to have been waterproofed and as, when the chloroform solution from the powder was just passing to dryness, a faint odor of nitrobenzene was discerned, it is possible that this agent, together with wood spirits was used superficially to produce this effect. The waterproofing was not, however, very efficient, for, after three hours immersion in cold water, the grains were found to be very much swollen, while the water was colored yellow, possessed the characteristic odor of the powder, and deposited aurin and nitrates on evaporation.

*S. R. Powder.*—This sample was marked "Smokeless (S. R.) Rifle Gunpowder made by the Smokeless Powder Company, Limited, at Barwick Works, Herts, England." This powder resembled the S. K. powder described above in color, odor, and

form of grain, except that the S. R. passed through No. 16 sieve (though much of it was smaller) and that the odor was very strong.

Analysis gave:

	Per cent.
Nitro-cotton .....	28.18
Gun cotton.....	46.97
Aurin (alkaline) .....	1.06
Barium nitrate .....	19.97
Potassium nitrate.....	2.35
Volatile .....	1.45
	<hr/>
	99.98

As with the S. K. powder these grains were disintegrated by immersion in cold water.

*Rifleite Gunpowder.*—This powder, which was manufactured by the Smokeless Powder Company, Limited, at Barwick Works, Herts, England, was described on the package as being made for use with the Magazine Rifle 303. It was in the form of nearly square flat grains having the color and luster of graphite and the odor of wood spirits, which had apparently been used in waterproofing the grains. This waterproofing was not, however, completely efficacious, since when the powder was first immersed in cold water a considerable portion of the graphite floated off and rose to the surface of the water, and when the moist powder was subsequently dried in a porcelain dish, the graphite adhered to the walls of the dish. When the graphite, which was a wholly superficial covering, was removed from the grains, they were found to be faintly yellow colored and translucent. The water used in this operation had acquired the odor of the powder and on evaporation to dryness it left a yellow residue.

The powder offered considerable resistance to the action of ether-alcohol, but the grains gradually swelled up, split into laminae and were eventually completely disintegrated after seventy-two hours exposure to ether-alcohol in the cold.

The coloring matter, which was quite soluble in ethyl alcohol, was rather insoluble in ether-alcohol, and on the addition of ether to the alcohol solution this coloring matter was precipitated in beautiful golden yellow plates, which were identified as a phenyl

amidoazobenzene,  $C_6H_5.N_2.C_6H_5.NH(C_6H_5)$ , the sulphonate of which is known in commerce as Manchester Yellow.

Analysis gave:

	Per cent.
Nitro-cotton .....	22.48
Gun cotton .....	74.16
Phenyl amidoazobenzene .....	2.52
Graphite .....	Trace
Volatile .....	0.84
Total .....	100.00

The grains were found to average 0.0638 inch in length, 0.0612 in width, and 0.0155 in thickness, though occasional ones were nearly double this length.

I am indebted to the courtesy of the New England representative of the U. S. Cartridge Company for these samples of powder from the Barwick works.

*Maxim Powder.*—I am indebted to the courtesy of Dr. J. E. Blömen, chemist to the Forcite Powder Company for two samples of this powder. The powder, which was evidently intended for use for small arm charges, was in two forms, one rectangular flat grains, and the other in short cords. The color was dark brown, the flat grains being somewhat translucent, while the cords were opaque. Both possessed a distinct fatty odor, but this was less marked and may have been accidental in the flat grains, as, when received, a few of the rods had become mixed with this sample. The flat grains were quite tough and offered considerable resistance to fracture, but the cord had very slight cohesive properties and fractured on application of slight force, like half dried putty.

A mean of the measurements of ten of the flat grains gave, length 0.0512 inch, width 0.459 inch, thickness 0.0166 inch.

Analysis gave:

	Per cent.
Nitro-cotton .....	8.14
Gun cotton .....	71.19
Sodium carbonate .....	2.58
Nitroglycerine .....	17.90
Volatile .....	0.19
	100.00

The average of the measurements of ten of the cord formed grains gave, length 0.25 inch, diameter 0.0456 inch. The ends of these grains were rough as if they had been broken from the rods, so the micrometer measurement for the lengths is only approximate.

Analysis gave:

	Per cent.
Nitro-cotton.....	6.84
Gun cotton.....	46.60
Nitroglycerine .....	44.60
Sodium carbonate .....	1.70
Volatile .....	0.26
	<hr/>
	100.00

The odor of castor oil was plainly distinguishable even in the cold, and when the powder was immersed in cold water for as short a time as three hours, the water became yellow colored and yielded a fatty residue on evaporation, but we have no good method as yet for separating this oil or resin quantitatively from nitroglycerine.

*German Smokeless Powder.*—This sample was received with the statement that it was a German powder procured from Cologne for trial in the 8" B. L. Rifle. The powder was in the form of nearly cubical grains about 1 cc. in volume and averaging 1.6203 grams each in weight. The surface had the luster and color of graphite and the cubes appear as if they had been cut from a larger mass with a saw. The grains were of such consistency that they could just be indented with the finger-nail. On cutting the grains, the graphitic appearance was found to be wholly superficial, the interior having the appearance of explosive gelatine, though having a greater consistency than the latter substance.

Analysis gave:

	Per cent.
Nitro-cotton.....	48.83
Gun cotton.....	7.45
Nitroglycerine.....	43.15
Graphite .....	Trace
Volatile .....	0.53
	<hr/>
	99.96

I am deeply indebted to Mr. G. W. Patterson for his valuable assistance in this work.

## THE DETERMINATION OF THE RELATIVE SENSITIVENESS OF EXPLOSIVE SUBSTANCES THROUGH "EXPLOSIONS BY INFLUENCE."

BY CHARLES E. MUNROE.

THE determination of the sensitiveness of explosive substances has already been made by a number of different methods, but it is yet a question as to the real value of these results. Thus, we have the methods by percussion, by heat, by friction, and the like. It has occurred to me that a much more delicate and reliable method would result from the employment of what has been termed by Berthelot "explosion by influence." What is meant by this term is the explosion of a secondary mass through the explosion of a primary mass which is separated from the secondary mass by a definite interval. Numerous observations have been made, as notably in the Danish experiments, in explosions of this kind taking place under water, and a great many instances are recorded of similar explosions being brought about on the surface of the earth; but the submarine experiments were made with a limited number of substances confined in envelopes which materially modified the results, while the earth experiments were made under continually varying conditions. In the experiments which I have to record I have employed a continuous and, as nearly as may be, homogeneous medium, through which the effect of the explosion of the primary mass is conveyed to the secondary mass, while I have used definite and moderate quantities of explosives under constant conditions of confinement—circumstances which are easily repeated, while the attending phenomena are easily observed.

The method pursued was as follows:

The initial and secondary masses were placed upon a wrought iron armor plate nine feet five inches long, three feet four inches wide, and one inch thick, which rested upon a second plate of the same material and dimensions. These plates had been made for use on vessels of war, and consequently they contained several lines of rivet holes and also were curved to

<sup>1</sup> Read at Newport General Meeting.

the shape of the vessel. This of course affected the rigidity of the system, and it was expected that it might introduce irregularities into the results, but firing trials made under otherwise similar conditions showed that for the masses of explosives used the results were uniform at all points.

The initial mass consisted of 100 grams of explosive, while the secondary mass varied from 30 to 100 grams, it being evident that the weight of the secondary mass had no effect on its sensitiveness, and that it was essential only to have a sufficient quantity to produce a positive and visible effect on the firing plate in case it was exploded.

In the experiments for testing the relative sensitiveness of different explosives when referred to a common standard, 100 grams of United States service gun cotton was selected for the initial mass because it was the most accessible, convenient, and constant one at hand, but apart from these considerations there is an advantage in using this as the initial mass, since it has been shown by Abel that gun cotton is the most efficient detonating priming agent among explosive substances.

The gun cotton, as issued from the Naval Torpedo Station where it is manufactured, is in the form of blocks two and nine-tenths inches in diameter, three and seven-eighths inches in diagonal (the corners being chamfered), and two inches in height, and it is made by compressing pulped gun cotton in molds by means of a hydraulic press, the pressure applied being about 6,500 pounds per square inch. The gun cotton when so pressed has a gravimetric density of 1.2871. It should be added that the blocks are pierced through the center with a hole seven-sixteenths inch in diameter in which the detonator is to be inserted for firing. This gun cotton was steam-dried before using, and pieces of 100 grams weight were cut off by cutting transversely to the vertical axis, so that the diameter of the base of these pieces was that of the blocks from which they were taken, or 7.4 centimeters.

As all the other explosives were in the form of either a powder or paste, it was necessary to provide containers for them, and these were made from well calendered manilla paper. When these explosives were used for the initial mass the boxes had



the same form and dimensions as the service block of gun cotton, except that the corners were not chamfered, and hence the area of the surface in contact with the plate was very closely the same as for the gun cotton. When these explosives were used as secondary masses they were enclosed in similar open paper boxes, but they were but 5.58 centimeters in diameter. In all cases the explosive was evenly distributed over the bottom of the case and brought well in contact with it, so that the area of the face of these different explosives in contact with the firing plate was as nearly as possible identical. It is evident from this description that the explosives were tested when unconfined except by atmospheric tamping.

In making the test it was of course necessary to proceed in a purely tentative manner. A point was selected upon the plate where no breaches of continuity were apparent for a considerable range, the initial mass was placed upon the plate and at the outset of each series two secondary masses (one being placed on either side of the initial or primary mass and at unequal distances from it) and the primary one detonated. When this was detonated it produced a well marked impression on the iron, and the same effect was observed in the case of the secondary masses when they were detonated, the effect, however, being in all cases diminished as the secondary mass approached that point at which it ceased to be detonated. The observations were most easily made when gun cotton was used for both the primary and secondary charges, for when the secondary charge was not far beyond the limit at which secondary charges could be detonated, it burst into flame and was tossed into the air in this inflamed condition through the disturbance produced in the atmosphere by the detonation of the initial mass.

When non-detonating or sub-detonating explosives were used for the secondary charges, impressions were produced so long as explosion was effected, but the impressions produced, at least near the extreme limit, were due only to the removal of scale from the plate by the shock of the explosion and to the deposition of soot and other products. When beyond this limit the explosive was found scattered upon the plate together with fragments of the containers.

As in the course of these experiments we appeared to approach the limit, single secondary charges only were used with each initial charge in order to simplify the observations. It should be added that the points measured were from the inside edge of the primary mass to the inside edge of the secondary mass before explosion.

The results obtained were as follows:

#### GUN COTTON ON GUN COTTON.

Initial mass, gun cotton.	Secondary mass, gun cotton.	Distance.	Result.
100 grams.	100 grams.	10 cm.	Detonated.
100 "	100 "	10 "	"
100 "	60 "	10 "	"
100 "	100 "	10.5 "	Failed.
100 "	60 "	11 "	"
100 "	100 "	11 "	"
100 "	100 "	12 "	"
100 "	100 "	17.3 "	"
100 "	100 "	35 "	"
100 "	100 "	70 "	"

#### GUN COTTON ON JUDSON POWDER, R. R. P.

Initial mass, gun cotton.	Secondary mass, gun cotton.	Distance.	Result.
100 grams.	30 grams.	20 cm.	Detonated.
100 "	30 "	20 "	"
100 "	30 "	25 "	"
100 "	30 "	25 "	"
100 "	30 "	26 "	Failed.
100 "	30 "	27 "	"
100 "	30 "	30 "	"

#### GUN COTTON ON EMMENSITE, No. 259.

Initial mass, gun cotton.	Secondary mass, Emmensite.	Distance.	Result.
100 grams.	60 grams.	10 cm.	Exploded.
100 "	60 "	11 "	"
100 "	60 "	12 "	"
100 "	60 "	13 "	"
100 "	60 "	14 "	"
100 "	60 "	15 "	"
100 "	60 "	16 "	"
100 "	60 "	17 "	"
100 "	60 "	20 "	"
100 "	60 "	25 "	"
100 "	60 "	30 "	"
100 "	60 "	31 "	Failed.
100 "	60 "	35 "	"
100 "	60 "	35 "	"
100 "	60 "	40 "	"

## EXPLOSIONS BY INFLUENCE.

## GUN COTTON ON EMMENSITE (259) II.

Initial mass, gun cotton.	Secondary mass, Emmensite II.	Distance.	Result.
100 grams.	60 grams.	30 cm.	Exploded.
100 "	60 "	31 "	"
100 "	60 "	31 "	Failed.
100 "	60 "	32 "	"

This Emmensite II is a portion of No. 259 which had been subjected to temperatures of 120° F. and 60° F. alternately for varying periods during sixty-three days.

The firing plate was exposed to the sun, and on the day of these experiments it was so hot that one could hardly hold the naked hand upon it, while in the previous experiments, the sky being overcast, the plate was not noticeably warm.

## GUN COTTON ON FORCITE NO. 1.

Initial mass, gun cotton.	Secondary mass, Forcite Powder.	Distance.	Result.
100 grams.	30 grams.	40 cm.	Detonated.
100 "	30 "	50 "	"
100 "	30 "	60 "	"
100 "	30 "	60 "	Doubtful.
100 "	30 "	61 "	"
100 "	30 "	62 "	Failed.
100 "	30 "	65 "	"
100 "	30 "	70 "	"

The forcite was well pressed down in the bottom of the paper box and the bottom of the latter appeared to be moistened by exuded nitroglycerine. The forcite, except in being transferred from the cartridge cases, was in the same condition as when purchased from the company.

## GUN COTTON ON ATLAS NO. 1.

Initial mass, gun cotton.	Secondary mass, Atlas Powder.	Distance.	Result.
100 gram.	30 grams.	20 cm.	Detonated.
100 "	30 "	30 "	"
100 "	30 "	40 "	"
100 "	30 "	50 "	"
100 "	30 "	60 "	"
100 "	30 "	70 "	"
100 "	30 "	71 "	"
100 "	30 "	72 "	"
100 "	30 "	73 "	Doubtful.
100 "	30 "	73 "	Detonated.
100 "	30 "	74 "	Failed.
100 "	30 "	75 "	"
100 "	30 "	80 "	"
100 "	30 "	90 "	"

The wind was strong from the southwest during these experi-

ments, and as double secondary charges were used in the earlier rounds, the more distant one being to southwest of the primary, there was an uncertainty in the first round at seventy-three and seventy-five cm. whether unexploded Atlas powder at the seventy-three cm. position to the northeast was a residue from this charge, or had been carried by the wind from the seventy-five cm. charge.

The Atlas charges were pressed firmly down in paper box and the latter appeared to be moistened by exuded nitro-glycerine.

#### GUN COTTON ON EXPLOSIVE GELATINE (CAMPHORATED).

Initial mass, gun cotton.	Secondary mass, Explosive Gelatine.	Distance.	Result.
100 grams.	10 grams.	10 cm.	Detonated.
100 "	10 "	15 "	"
100 "	10 "	18 "	"
100 "	10 "	20 "	"
100 "	10 "	21 "	Failed.
100 "	10 "	60 "	"
100 "	10 "	66 "	"

This explosive gelatine was made at the United States Naval Torpedo Station at Newport, R. I., March 31, 1889, and consisted of nitroglycerine 86.5 per cent., nitro-cotton 9.6 per cent., camphor 4 per cent., and was tested August 2, 1890.

#### GUN COTTON ON BELLITE.

Initial mass, gun cotton.	Secondary mass, Bellite.	Distance.	Result.
100 grams.	30 grams.	50 cm.	Detonated.
100 "	30 "	50 "	"
100 "	30 "	51 "	Failed.
100 "	30 "	53 "	"
100 "	30 "	55 "	"
100 "	30 "	60 "	"
100 "	30 "	100 "	"

This bellite was made January 21, 1890, by fusing together  $\text{NH}_4\text{NO}_3$  five parts;  $\text{C}_2\text{H}_5(\text{NO}_2)$ , (1 : 3), one part, and was tested August 2, 1890.

#### GUN COTTON ON KIRSELGUHR DYNAMITE NO. 1.

Initial mass, gun cotton.	Secondary mass, Kieselguhr dynamite.	Distance.	Result.
100 grams.	30 grams.	30 cm.	Detonated.
100 "	30 "	40 "	"
100 "	30 "	40 "	"
100 "	30 "	50 "	"
100 "	30 "	50 "	"
100 "	30 "	60 "	"
100 "	30 "	60 "	"

## GUN COTTON ON KIESELGUHR DYNAMITE NO. 1. (CONCLUDED).

Initial mass, gun cotton.	Secondary mass, Kieselguhr dynamite.	Distance.	Result.
100 grams.	30 grams.	63 cm.	Detonated.
100 "	30 "	64 "	"
100 "	30 "	65 "	Failed.
100 "	30 "	70 "	"
100 "	30 "	70 "	"
100 "	30 "	80 "	"

This 75 per cent. Kieselguhr dynamite was made at the United States Naval Torpedo Station at Newport, R. I., in 1884, and tested August, 1890.

## GUN COTTON ON RACKAROCK.

Initial mass, gun cotton.	Secondary mass, Rackarock.	Distance.	Result.
100 grams.	30 grams.	30 cm.	Detonated.
100 "	30 "	30 "	"
100 "	30 "	31 "	"
100 "	30 "	31 "	"
100 "	30 "	32 "	"
100 "	30 "	32 "	"
100 "	30 "	33 "	Failed.
100 "	30 "	33 "	"
100 "	30 "	40 "	"

This rackarock was made at the Naval Torpedo Station at Newport, R. I., in July, 1888, and consisted of  $\text{KClO}_3$ , seventy-nine parts;  $\text{C}_6\text{H}_5(\text{NO}_2)$  (sp. gr. 1.33), twenty-one parts; and was tested August, 1890.

Summing up this data we find that the relative sensitiveness of these explosives to detonating gun cotton, all being in the open and on the same iron plate, is as follows:

## RELATIVE SENSITIVENESS TO DETONATION BY GUN COTTON.

	Cm.
Gun cotton .....	10
Explosive Gelatine (camphorated) .....	20
Judson, R. R. P. ....	25
Emmensite (No. 259) .....	30
Rackarock .....	32
Bellite .....	50
Forcite No. 1 .....	61
Kieselguhr Dynamite No 1 .....	64
Atlas No. 1 .....	74

These results are rather unexpected as it was supposed that the nitro-substitution explosives, emmensite, rackarock, and bellite would prove much less sensitive than camphorated explosive gelatine and Judson powder or even than gun cotton itself. The dynamites came out in their proper position

according to theory, though the relative position of the different ones might vary with different manufactured lots.

It is very important for practical operations in countermining to know if a similar difference exists in the relative sensitive-ness of different explosives to detonation by a single kind of priming substance, and this point should be thoroughly investigated.

Besides the above a few experiments were made to determine the greatest distance at which a unit mass of a substance could effect the explosion or detonation of a secondary mass of the same substance. The results are as follows:

EMMENSITE NO. 259 ON EMMENSITE NO. 259.

Initial mass.	Secondary mass.	Distance.	Result.
100 grams.	30 grams.	10 cm.	Exploded.
100 "	30 "	10 "	"
100 "	30 "	10 "	"
100 "	30 "	10 "	"
100 "	30 "	11 "	Failed.
100 "	30 "	15 "	"
100 "	30 "	15 "	"
100 "	30 "	20 "	"
100 "	30 "	20 "	"
100 "	30 "	30 "	"

ATLAS NO. 1 ON ATLAS NO. 1.

Initial mass.	Secondary mass.	Distance.	Result.
100 grams.	30 grams.	11 cm.	Exploded.
100 "	30 "	12 "	"
100 "	30 "	13 "	"
100 "	30 "	20 "	"
100 "	30 "	30 "	"

FORCITE NO. 1. ON FORCITE NO. 1.

Initial mass.	Secondary mass.	Distance.	Result.
100 grams.	30 grams.	11 cm.	Detonated.
100 "	30 "	14 "	"
100 "	30 "	14.5 "	"
100 "	30 "	15 "	"
100 "	30 "	15 "	Failed (?)

KIESELGUHR DYNAMITE NO. 1 ON KIESELGUHR DYNAMITE NO. 1.

Initial mass.	Secondary mass.	Distance.	Result.
100 grams.	30 grams.	11 cm.	Detonated.
100 "	30 "	15 "	"
100 "	30 "	20 "	"
100 "	30 "	25 "	"
100 "	30 "	30 "	"

These experiments were conducted like those in which gun cotton was used as the initial mass, except that both the initial and secondary masses were enclosed in paper boxes.

At this point I was compelled to cease the experiments and have not since been able to renew the work, but I believe that if these observations could be extended they would prove fruitful not only in interesting but practical results. However, the observer must have had a large experience in explosive work and the effects of explosives, or he will frequently be deceived as to the nature of the results obtained.

### THE ACTION OF THE HALOID ACIDS IN GAS FORM UPON MOLYBDIC ACID.

BY EDGAR F. SMITH AND VICKERS OBERHOLTZER.

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Debray (*Compt. rend.*, 46, 1098, and *Ann Chem. (Liebig)* 108, 250) first called attention to the fact that a very volatile, crystalline compound of the formula  $\text{MoO}_3 \cdot 2\text{HCl}$  resulted upon exposing molybdic acid heated from  $150^\circ$  to  $200^\circ$  to the action of hydrochloric acid gas. It is true that the constitution of this volatile product may also be represented by the formula  $\text{MoO}(\text{OH})\text{Cl}$ , which would make it a molybdenum hydroxychloride. Dismissing the question of constitution for the present and considering the point of easy volatility, it seemed to us that this behavior might be utilized for the separation of molybdic acid from tungstic acid, as the latter apparently does not enter into volatile combination with hydrochloric acid gas. We therefore exposed weighed amounts of sublimed molybdic acid to the action of the acid gas and succeeded in expelling the molybdic acid completely from the porcelain boats containing it. Applying the same treatment to what we considered pure tungstic acid we were greatly surprised to find that very appreciable quantities of a sublimate similar in every respect to that of molybdenum hydroxychloride was expelled from the boat. An examination of this product proved it to be the molybdic acid compound. In short our tungstic acid was not pure. We, however, continued to heat portions of it in hydrochloric acid gas until a sublimate was no longer obtained, when on mixing molybdic acid in known amount with the residual tungstic acid we discovered that we could completely expel the former acid from the latter. Our next step was to observe the

effect of heating dry sodium molybdate in hydrochloric acid gas. The appended results show a quantitative conversion into sodium chloride, consequently a complete volatilization of the molybdic acid.

Na <sub>2</sub> MoO <sub>4</sub> .	NaCl.	NaCl req'd.
0.1302 gram gave at 150–200°.....	0.0738	0.0739
0.1832 " " " " .....	0.1038	0.1040
0.2046 " " " " .....	0.1159	0.1162
0.3845 " " " " .....	0.2186	0.2183

As we were on the point of applying the method to the quantitative separation of molybdic acid and tungstic acid, both present as sodium salts, a closer scrutiny of the existing literature relating to the subject revealed that E. Péchard (*Compt. rend.*, 114, 173, and *Ztschr. anorg. Chem.*, 1, 262) had already carried out the determination of molybdic acid and its separation from tungstic acid in this way with very evident success. Our own experiments confirm those of Péchard in every particular.

As previously observed, the tungstic acid that we considered pure contained molybdic acid. Traube (*Neues Jahrbuch für Mineralogie, Geologie and Paleontologie, Beilage, Band 7*, 232) has demonstrated that natural calcium tungstate (scheelite) and commercial tungstic acid, obtained from the mineral wolframite, contain molybdic acid. E. Corleis (*Ann. Chem. (Liebig)*, 232, 265) has shown that the latter acid is even present in the "wolframsäure puriss" of trade, while Friedheim (*Ztschr. anorg. Chem.*, 1, 76) asserts that commercial sodium tungstate is strongly contaminated with sodium molybdate, and that even when exercising the greatest care in the process of purification the tungstate continued to show traces of molybdenum.

We found molybdic acid present in the purest sodium tungstate that we could get, and in the minerals scheelite and wolframite when these were exposed to the action of hydrochloric acid gas at a temperature not exceeding 400° C. We, therefore, are inclined to regard this method as excellently adapted for the detection of molybdic acid as well as for the purification of tungstic acid and tungstates containing molybdenum.

Our original purpose having been the study of the behavior of molybdic acid in atmospheres of all the gaseous haloid acids, we may now briefly recount our experience in those directions.



*Action of Hydrobromic Acid, in Gas Form, upon Molybdic Acid.*—The molybdic acid used by us was purified by converting the commercial acid into the ammonium salt, which was recrystallized a number of times and then ignited with access of air. The product was sublimed very carefully from a platinum crucible. The hydrobromic acid gas was prepared by dropping bromine from a separatory funnel upon crude anthracene contained in a half-liter flask. It passed through a hard glass tube six inches in length, filled with anthracene, then through the anthracene, then through two U tubes containing a paste of amorphous phosphorus and two U tubes provided with fused calcium chloride, while the sixth or last tube contained phosphoric anhydride. Having completed this circuit it was admitted to a perfectly dry combustion tube into which there had been introduced a porcelain boat filled with molybdic acid. The anterior end of the combustion tube was provided with a calcium chloride tube to exclude all moisture. The heat used in the experiment was applied from a combustion furnace. An ordinary thermometer was placed above the combustion tube, its bulb rested directly above the boat. In this manner we recorded the approximate temperature at which the reaction took place. As soon as the entire apparatus was filled with the gas, three burners of the furnace, directly under the boat, were lighted, and the heat raised gradually until it reached 200° C. A change took place almost instantly. Immediately beyond the boat appeared a heavy sublimate with a color resembling that of permanganate of potassium. Beyond this solid a brownish yellow colored liquid separated; on cooling it changed to long, beautiful yellow needles. These proved to be very unstable, melting almost immediately when brought in contact with the air. At the expiration of an hour the passage of the hydrobromic acid gas was interrupted. The permanganate-colored sublimate was removed from the sides of the tube as completely as possible, introduced into a porcelain boat, and then carefully resublimed in a current of dry carbon dioxide.

The compound sublimed in fern-like aggregates of beautiful dark red or purple red, shining, overlapping plates, extending from side to side of the combustion tube. They dissolved in

water with evolution of heat. Their aqueous solution was colorless, but upon standing became blue in color. The crystals also changed on prolonged exposure to the air. By bringing them into well corked bottles filled with carbon dioxide, they were preserved without undergoing decomposition. An examination of the crystals under a polarizing microscope showed them to be capable of polarizing light, and that they consisted of aggregations of perfectly square plates. After the resublimation portions of the substance were weighed off in closed weighing tubes and analyzed. For the determination of the bromine the material was dissolved in as little cold water as possible, dilute nitric acid added, and this followed immediately by the addition of silver nitrate. The resulting silver bromide was treated in the usual manner. In estimating the molybdenum the substance was brought into a weighed porcelain crucible and dilute nitric acid added. The solution was evaporated almost to dryness at a very gentle heat, when the crucible contents were treated with concentrated nitric acid, after which followed evaporation to perfect dryness. This operation was repeated, and a gentle but direct heat applied to the crucible for periods varying from one-half to one hour. This was done in order to completely oxidize the molybdenum to trioxide. To ascertain whether the new compound contained water, portions of it were mixed with freshly ignited litharge and heated in a current of dry air, using a perfectly dry combustion tube provided with a weighed calcium chloride tube. The weight of the latter showed no increase, so that we were safe in considering our substance free from hydrogen.

## ANALYSIS.

**Bromine determination:**

		AgBr.	Per cent. Br.
No. 1.	0.1334 gram substance gave.....	0.1793 gram	59.19
No. 2.	0.3353 " " " .....	0.4499 "	57.09
No. 3.	0.0680 " " " .....	0.0908 "	56.82

The mean of these bromine percentages is 57.03 per cent.

**Molybdenum determination:**

		MoO <sub>3</sub>	Per cent. Br.
No. 1.	0.2545 gram substance gave.....	0.12865 gram	33.69
No. 2.	0.2916 " " " .....	0.1466 "	33.52
No. 3.	0.1115 " " " .....	0.0559 "	33.42

The mean of the molybdenum percentages is 33.54 per cent.

We experienced great difficulty in wholly eliminating the traces of "blue oxide" in all our determinations of the molybdenum, hence we look upon these results as low.

Regarding, then, our compound as consisting of molybdenum, bromine, and oxygen with the above percentages, taking the oxygen by difference, we deduce as the most probable formula:  $\text{MoO}_3\text{Br}_2$ ,  $\text{MoOBr}_2$ , or  $\text{Mo}_2\text{O}_5\text{Br}_2$ —molybdenum sesquioxide tetrabromide. The theoretical requirements of this formula are 34.28 per cent. Mo, 57.14 per cent. Br, and 8.57 per cent. O.

The only existing molybdenum oxybromide until the present time has been  $\text{MoO}_3\text{Br}_2$ —molybdenyl bromide, discovered by Blomstrand in passing bromine vapor over the heated dioxide of molybdenum, or by heating a mixture of molybdic acid and borax with potassium bromide. It is mentioned as forming yellow deliquescent tablets. For the sake of comparison we prepared the compound of Blomstrand by the second method. We found that when it sublimed upon a previously heated portion of the tube, it separated in "mehr ausgebildeten Krystalltafeln auf; bei rascher Sublimierung in undeutlich krystallinischen Schuppen. Farbe schön gelbroth" (Blomstrand, *J. prakt. Chem.*, **82**, 439). Our compound, however, is formed simultaneously with that of Blomstrand when bromine vapors are conducted over heated molybdic acid. The tube in which this reaction was made was first freed from air by conducting bromine vapor through it, and heat was not applied until we were satisfied that bromine alone was present.

The brownish yellow liquid, formed at the same time with the purple red colored solid, was crystallized in the tube in which it was formed. The tube was then severed at a point between the yellow and red colored compounds. The yellow immediately liquefied on exposure to the air. The liquid was collected in a small beaker previously weighed. This was then placed in a sulphuric acid desiccator, and the air exhausted. At the expiration of two or three days the yellow needles had reformed. The beaker and its contents were then rapidly weighed. Water was poured on the needles. Their solution was colorless, or slightly yellow tinged. On standing, the

liquid slowly acquired a deeper yellow, or reddish yellow hue, and after twenty-four hours a "blue oxide" of molybdenum had separated. The bromine and molybdenum were determined in this product in the same manner as in the purple colored solid. We, however, experienced no difficulty in obtaining perfectly white molybdic acid in all of our analyses.

## ANALYSIS.

## Bromine determination :

		AgBr.	Per cent. Br.
No. 1.	0.0950 gram substance gave.....	0.1403 gram	62.83
No. 2.	0.2523 " " " .....	0.3700 "	62.50
No. 3.	0.2709 " " " .....	0.3967 "	62.37
No. 4.	0.0250 " " " .....	0.0365 "	62.12

The mean of these determinations is 62.45 per cent. Br.

## Molybdenum determination :

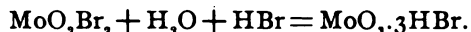
		AgBr.	Per cent. Br.
No. 1.	0.0946 gram substance gave.....	0.0346 gram	24.39
No. 2.	0.0946 " " " .....	0.0337 "	23.75
No. 3.	0.1892 " " " .....	0.0686 "	24.06

The mean percentage of molybdenum found is 24.03 per cent.

The formula that we deduce from these results is  $\text{MoO}_3.3\text{HBr}$ .

It might be represented better, perhaps, as a trihydroxybromide,  $\text{Mo}(\text{OH})_3\text{Br}_3$ . The theoretical requirements in either case are 62.02 per cent. Br and 24.80 per cent. Mo.

It is interesting to note that the long, yellow colored needles of this compound were also obtained upon passing hydrobromic acid gas over the oxybromide of Blomstrand at a gentle heat. This change may easily be conceived as occurring, if we grant the presence or production of water through the formation of secondary products:



As we were not in a position to ascertain the true composition of the residual substance or substances from scarcity of material, we offer the suggestion as a possible explanation for the appearance of the hydroxybromide in the manner above indicated.

*Action of Hydriodic Acid, in Gas Form, upon Molybdic Acid.*—

A violent reaction occurred in the cold, upon passing the dry acid gas over molybdic acid. Much heat was evolved, and iodine was liberated. The non-volatile product that re-





towards the light, it appeared to be filled with violet vapors of iodine. This was due, however, to reflection of light from the sides of the flat, needle-like crystals. It is scarcely necessary to remark that before disconnecting the apparatus carbon dioxide was conducted through it to expel the hydrofluoric acid gas. The platinum flask also contained the volatile molybdenum product. Much hydrofluoric acid was with it. This was expelled by the introduction of carbon dioxide.

The new product, when removed from the vessels containing it, was found to be deliquescent, and gradually decomposed into a blue oxide of molybdenum. It attacked glass, was insoluble, or nearly insoluble, in water, but dissolved to a colorless liquid in hydrofluoric acid, and was left undecomposed on evaporation. Portions of it were weighed off as rapidly as possible in platinum crucibles, and the molybdenum determined as trioxide by evaporation with nitric acid, followed by gentle ignition.

## ANALYSIS.

## Molybdenum determination:

		MoO <sub>3</sub> .	Per cent. Mo.
No. 1.	0.0526 gram substance gave.....	0.0479 gram	60.70
No. 2.	0.1066 " " " " .....	0.0967 "	60.66
No. 3.	0.1166 " " " " .....	0.1051 "	60.94
No. 4.	0.1265 " " " " .....	0.1164 "	61.35

The mean of these determinations is 60.91 per cent.

Formed in the same manner as molybdenum sesquioxide tetrabromide, we find that these results agree very closely with an oxyfluoride of an analogous formula,  $\text{Mo}_2\text{O}_3\text{F}_2$ , which would require 60.76 per cent. of molybdenum.

In our experiments with the above oxyfluoride, we several times observed a slight quantity of a colorless liquid, which, upon careful evaporation with nitric acid, left a very appreciable amount of molybdic acid. In this compound of molybdenum, we may, perhaps, have an analogue of the very volatile  $\text{MoO}_3 \cdot 2\text{HCl}$ , and the liquid, unstable  $\text{MoO}_3 \cdot 3\text{HBr}$ . We endeavored to fix its composition, but experienced so much difficulty in obtaining material that we could regard as sufficiently pure, that we abandoned it entirely. The work attending its preparation is anything but pleasant, and the yield exceedingly uncertain.

Only one other oxyfluoride of molybdenum is known, namely that prepared by Schulze (*J. prakt. Chem.*, **21**, N. F., 442), by fusing metallic fluorides together with molybdic acid with the exclusion of air. It has the constitution expressed by the formula  $\text{MoO}_3\text{F}_2$ .

Reviewing, then, the action of the gaseous haloid acids upon molybdic acid, we find, first, that hydrochloric acid converts the acid into a solid, very volatile product,  $\text{MoO}_3 \cdot 2\text{HCl}$ ; second, that hydrobromic acid changes molybdic acid to a volatile brownish yellow liquid,  $\text{MoO}_3 \cdot 3\text{HBr}$ , forming long yellow needles at low temperatures and under diminished pressure, and a beautifully crystallized solid of the formula  $\text{MoO}_3\text{Br}_2 \cdot \text{MoOBr}_2$ ; third, that hydriodic acid reduces molybdic acid to a new oxide,  $\text{Mo}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ; fourth, that hydrofluoric acid converts molybdic acid into at least one well formed, but volatile, product, having approximately the formula  $\text{MoO}_3\text{F}_2 \cdot \text{MoOF}_3$ , or  $\text{Mo}_2\text{O}_5\text{F}_4$ .

Püttbach (*Ann. Chem.*, (*Liebig*), **201**, 137) divides the known molybdenum oxychlorides into two classes:

Saturated	and	Unsaturated.
$\text{MoOCl}_4$		$\text{Mo}_2\text{O}_5\text{Cl}_7$
$\text{Mo}_2\text{O}_5\text{Cl}_6$		$\text{Mo}_2\text{O}_5\text{Cl}_4$
$\text{Mo}_2\text{O}_5\text{Cl}_5$		.....
$\text{MoO}_2\text{Cl}_2$		.....

But one oxybromide, already mentioned, is known. Its formula is  $\text{MoO}_3\text{Br}_2$ . Our experiments add to this the compound  $\text{Mo}_2\text{O}_5\text{Br}_2$ , which would correspond to  $\text{Mo}_2\text{O}_5\text{Cl}_4$ . The latter is light brown in color. Schulze's oxyfluoride would correspond to  $\text{MoO}_2\text{Cl}_2$  and  $\text{MoO}_3\text{Br}_2$ , while that obtained by us corresponds to  $\text{Mo}_2\text{O}_5\text{Cl}_4$  and  $\text{Mo}_2\text{O}_5\text{Br}_2$ . Püttbach's division presupposes the presence of a sexivalent molybdenum atom in the saturated members, while the unsaturated are regarded as derived from two molecules of  $\text{MoCl}_5$  by the substitution of oxygen for equivalent amounts of chlorine. Our oxybromide  $\text{Mo}_2\text{O}_5\text{Br}_2$  and oxyfluoride  $\text{Mo}_2\text{O}_5\text{F}_4$  may be looked upon as possessing similar origin, although their corresponding penta-bromide and pentafluoride are unknown.

The compound  $\text{MoO}_3 \cdot 3\text{HBr}$ , like  $\text{MoO}_3 \cdot 2\text{HCl}$ , presupposes



the presence of a sexivalent molybdenum atom, and may be properly considered a hydroxybromide represented thus— $\text{Mo}(\text{OH})_6\text{Br}_6$ —a derivative of the unknown hexabromide.

UNIVERSITY OF PENNSYLVANIA,  
CHEMICAL LABORATORY.

## THE ELECTROLYTIC SEPARATION OF MERCURY FROM BISMUTH.

BY EDGAR F. SMITH AND J. BIRD MOYER.

The question as to whether mercury can be completely precipitated by the current in the presence of nitric acid has been frequently discussed and answered in the affirmative. We observe, too, that in electrolytic literature it is this solution of mercury which has been generally recommended for the separation of the latter metal from various other metals associated with it. Thus, in the latest edition (the third) of Classen's *Quantitative Analyse durch Elektrolyse*, p. 147, the author, in describing the analysis of an alloy containing tin, lead, bismuth, and mercury, writes as follows:

"Aus der salpetersauren Lösung (the filtrate from the tin oxide) kann man nun zunächst das *Quecksilber* und einen Theil des Bleies als Superoxyd auf der positiven Elektrode fällen. Um die vollständige Abscheidung des Bleies zu bewirken unterwirft man die von Quecksilber befreite Lösung nochmals der Elektrolyse, indem man die Schale mit dem positiven Pol des Stromerzeugers verbindet, verdampft zur Bestimmung des *Wismuths* die bleifrei Lösung zur Trockne und verfährt nach S. 81," etc., etc.

These instructions would most certainly lead one to infer that mercury can be separated in the electrolytic way from bismuth in the presence of nitric acid. Trials, qualitative it is true, were made by one of us (S) years ago; these indicated a co-precipitation of the metals from a nitric acid solution, and therefore we find in Smith's *Electrochemical Analysis*,<sup>1</sup> p. 97, the statement that "mercury cannot be separated in the electrolytic way from silver and bismuth." The recent experience of Smith and Saltar<sup>2</sup> with

<sup>1</sup> W. Brinton, Son & Co., Philadelphia, Pa.

<sup>2</sup> *Anal. Appl. Chem.*, 7, 126.

copper and bismuth confirms this last observation. That others may be convinced that these two metals—mercury and bismuth—cannot be separated electrolytically, when present in a nitric acid solution, we submit the results obtained lately.

We first experimented upon the solution of a mercury salt. It contained 0.1132 gram of metallic mercury in ten cc. of liquid.

*Experiment 1.*

To ten cc. mercury solution (=0.1132 gram of metallic mercury) were added five cc. of nitric acid (sp. gr. 1.2), and then diluted with water to 180 cc. A current of 0.6 cc. electrolytic gas per minute was permitted to act upon this solution. The deposit of mercury weighed 0.1132 gram.

*Experiment 2.*

The quantity of metallic mercury was the same as in experiment 1. The volume of nitric acid (sp. gr. 1.2) was three cc.; the total dilution equaled 180 cc., and the current liberated 0.3 cc. electrolytic gas per minute. The precipitated mercury weighed 0.1137 gram.

*Experiment 3.*

The conditions were the same as in the preceding experiment, except that the volume of acid added equaled ten cc. and the current gave 0.3 cc. electrolytic gas per minute. The deposit of mercury weighed 0.1131 gram.

*Experiment 4.*

In this instance the only departure from the conditions observed in the preceding experiment was that fifteen cc. of acid were added to the solution undergoing electrolysis. The deposited mercury weighed 0.1131 gm. In appearance it was more drop-like than any of the previous deposits.

*Experiment 5.*

The conditions of experiments 3 and 4 were retained, but the volume of acid was increased to twenty-five cc. The precipitated mercury weighed 0.1083 gm. The filtrate showed the presence of unprecipitated metal. A second trial proved just as unsuccessful, but upon raising the current to one cc. electrolytic gas per minute, in two later experiments, with conditions otherwise the

same as indicated above, the quantities of metal precipitated were

a .....	0.1130 gram.
b .....	0.1130 "

The precipitation was complete. We see, however, from the above that as the quantity of free acid is increased it is well to increase the strength of the acting current.

It will be understood that the current strength mentioned by us in this article was that with voltameter and the electrolyte in circuit.

The deposits of mercury were washed with warm water and alcohol. They were dried by holding the dish in the hand and blowing gently over the metal surface, and also by standing over sulphuric acid for a brief period.

The bismuth solution employed by us was of such strength that ten cc. of it contained 0.1432 gram of metallic bismuth. The conditions of complete precipitation of this metal from nitric acid solution have already been given by Smith and Saltar.<sup>1</sup> We can therefore advance to an account of our experience in attempting to separate these metals.

#### *Experiment 1.*

Ten cc. of mercury solution (=0.1132 gram of metallic mercury), five cc. of bismuth solution (=0.0716 gram of metallic bismuth), and ten cc. of nitric acid of sp. gr. 1.2, were diluted to 200 cc, and electrolyzed with a current that gave 0.4 cc. of electrolytic gas per minute. The weight of precipitated metal was 0.1821 gram. The anode was also covered with bismuth peroxide. The precipitation of metals was complete, but the mercury contained bismuth.

#### *Experiment 2.*

Preserving the conditions of experiment 1, but increasing the volume of acid to fifteen cc., the weight of the metallic deposit was 0.1850 gram. The anode also showed bismuth. Thus, again, *this metal appeared at both poles.*

#### *Experiment 3.*

Here the volume of acid was increased to twenty-five cc. and

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, 128.

the current lowered to 0.2 cc. electrolytic gas per minute. The precipitation of metals was incomplete, although bismuth was found at both poles. On repeating the experiment the precipitation was found to be incomplete.

*Experiment 4.*

The current was increased to 0.8 cc. electrolytic gas per minute. The precipitation was complete, but bismuth appeared at both poles.

*Experiment 5.*

In this experiment we observed the following conditions:

Ten cc. of mercury solution ( $=0.1132$  gram of metallic mercury), two cc. of bismuth solution ( $=0.0358$  gram of metallic bismuth), twenty-five cc. of nitric acid (sp. gr. 1.3), and total dilution of 180 cc., were electrolyzed with a current liberating 1.5 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1441 gram. The positive pole was covered with bismuth peroxide. The mercury contained metallic bismuth. The precipitation of metals was complete.

*Experiment 6.*

With conditions the same as those of experiment 5 the precipitated mercury weighed 0.1445 gram; the anode was covered with bismuth peroxide.

*Experiment 7.*

In this trial the only change that we made from the conditions of experiment 6 was to reduce the quantity of bismuth to 0.0179 gram. The precipitated mercury weighed 0.1290 gram. It showed bismuth. The anode was coated with bismuth peroxide. The precipitation of metals was complete.

*Experiment 8.*

With conditions similar to those of 7, except that the current registered 1.4 cc. of electrolytic gas per minute, the precipitated mercury weighed 0.1284 gram. The anode showed bismuth peroxide. We found that the metals were precipitated simultaneously. Indeed, at times, it seemed that the precipitation of the bismuth began before that of the mercury. This was true with the most varying conditions. Hence, we believe that the

conditions proposed by Classen (see quotation above) should be modified to accord with facts, as stated by us, and with his own personal observation, as recorded in the *Ber. d. chem. Ges.* (1886), **19**, 325:

“Von *Wismuth* konnte das Quecksilber auf diese Weise nicht getrennt werden. Beide Metalle scheiden sich gleichzeitig aus der sauren Lösung aus.”

CHEMICAL LABORATORY OF  
THE UNIVERSITY OF PENNSYLVANIA.  
1893.

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## THE ELECTROLYTIC SEPARATION OF COPPER FROM ANTIMONY.

BY EDGAR F. SMITH AND D. L. WALLACE.

The separation of these two metals, in the electrolytic way, has long presented difficulties. These were first noticed by Wrightson (*Ztschr. anal. Chem.*, **15**, 297). Operating upon solutions containing 1.2075 per cent. of metallic copper and 0.280 per cent. to 0.800 per cent. of antimony, in the presence of twenty cc. of nitric acid of sp. gr. 1.21, and total dilution of 200 cc., he found that more or less antimony was precipitated together with the copper. Wrightson remarks, however, that in the presence of much less antimony (*e. g.*, in impure copper) it is possible to throw down the copper free from antimony. Classen corroborates this statement, and finds that the separation of copper and antimony may be made in a solution of the double oxalates (*Quantitative Analyse durch Elektrolyse*, dritte Auflage, p. 125), provided that the antimony content is very slight, and that the current is not permitted to act any longer than absolutely necessary for the complete decomposition of the copper.

From the preceding statements it is manifest that a better, more certain, separation is desirable. In conjunction with Muhr (*J. Anal. Appl. Chem.*, **5**, 488) one of us (S) found that iron, cadmium, copper, nickel, and other metals could be completely precipitated from ammoniacal tartrate solutions. The iron carried down carbon with it; this was not the case with the other

metals. Antimony, it was discovered, could also be deposited from an ammoniacal and alkaline tartrate solution quite rapidly, but after it had been converted into a higher oxide by means of bromine, and its solution then mixed with tartaric acid and ammonia sufficient to render it strongly alkaline it was no longer precipitated by the current. With this difference in behavior toward the current before us we combined copper and antimony solutions in the presence of tartaric acid and ammonia, then electrolyzed the same. The results we obtained show that the separation is possible and very satisfactory. We purposely varied the quantities of the two metals to render it certain that we could rely upon the method even under varying conditions.

	Copper present in grams.	Antimony present in grams.	Current in cc. O-H gas per minute.	Total dilution cc.	Copper found in grams.
1.	0.1341	0.1087	1.4	175	0.1341
2.	0.1341	0.1449	1.4	175	0.1343
3.	0.1341	0.2898	0.8	175	0.1344
4.	0.1341	0.1449	1.0	175	0.1340
5.	0.0134	0.1449	1.0	175	0.0142
6.	0.0268	0.1449	1.0	175	0.0274
7.	0.0670	0.1449	1.0	175	0.0670
8.	0.1341	0.1449	1.0	175	0.1341
9.	0.1341	0.1449	1.0	175	0.1341

The volume of ammonia present in each of these determinations equaled fifteen cc. (sp. gr. 0.932). The tartaric acid varied from three to four grams. The dishes in which the copper was precipitated ranged in weight from sixty to seventy grams. An examination of the deposited metal showed no antimony. It may be remarked that the strength of current maintained in these determinations was that indicated by the voltameter before the introduction of the electrolyte into the circuit of decomposition.

## THE RIVER NILE.

BY H. DROOP RICHMOND, LATE SECOND CHEMIST TO THE EGYPTIAN GOVERNMENT.

### I. INTRODUCTION.

The river Nile, the water-way of Egypt, is chiefly fed by the great equatorial rains; it drains an enormous area of northeast and northeast-central Africa, and reaches from about  $4^{\circ}$  south latitude to  $31^{\circ}$  north latitude, and runs, broadly speaking, south to north.

The Nile proper does not exist before Khartoum is reached; south of this it is composed of (a) the White Nile, (b) the Blue Nile, into which runs just above Berber the (c) Atbara or Black Nile. These names do not indicate the color of the water, but rather the intensity of the color due to suspended matter, and afford an instance of the figurativeness of Oriental language.

(a) The White Nile has its sources in the three great lakes, the Victoria, Albert, and Albert Edward Nyanzas, and receives the waters chiefly from the northern and eastern sides of the snow-clad mountains by means of many small tributaries; it passes for some distance after leaving the lakes through a marshy country, and here takes up a considerable quantity of vegetable matter, to which the green color noticed just before the flood is due; some of its tributaries, notably the Saubat, contain carbonate of calcium in suspension, and to this its name of White Nile has been ascribed by many, though it owes its name more to its comparative cleanness and freedom from suspended matter.

(b) The Blue Nile drains the southern side, (c) the Atbara the northern side, of the Abyssinian mountains; they are both of the same character, and contain large quantities of mud in suspension, especially in flood time, and to this, which imparts a dark red-brown color to the water, are the names Blue and Black Nile due.

All three rivers rise in the spring, the White Nile to a less extent than the others; except during this rise the water of the Blue Nile is small in amount compared with that in the White, which has large reservoirs in the lakes; this comparative constancy of the White Nile prevents the Nile in Egypt from sinking

into insignificance. The rise of the White Nile always takes place before that of the Blue, and the first symptom of this is the carrying down of its more or less stagnant waters of a greenish hue, which reach Cairo about the months of June or July, and cause the Nile water to be at its worst at that period; about a month afterwards the Blue Nile rises enormously and carries down with it immense quantities of suspended mud, and it is to this rise that the flood of the Egyptian Nile is due.

The two rivers join at Khartoum, and run for miles side by side with a fairly sharp line of demarcation, distinguished by the difference of color of the two waters; it flows thence over four "cataracts" or rather rocky parts to Wady





Halfa, where it enters Egypt, and at which point the present research commenced; near Wady Halfa is the second and largest cataract, and from then it continues to the first cataract at Assouan, where is a Nilometer or *gauge* of the height of the river, from the readings of which the state of the flood is *gauged*; flowing past Edfoo, where is another Nilometer, (now disused, but of great interest as having furnished the clue to the length of the Nile "pic" or "drâa," the measure of the ancient Egyptians; c. f. Moukhtar Pasha, *Etudes sur les Mesures Egyptiennes*, Cairo, 1890), and Keneh, it reaches Assiout, where the Ibrahimieh canal leaves the river, to become at Deyrout the Bahr Yousef, or Yousefy River, which waters the Fayoum, and ends in the Birket-el-Kâm, often called Lake Moeris, but probably not the lost Lake Moeris, which was farther south. From Assiout, it flows past Minieh and Beni-Souef, to Cairo, where on the southern end of the Island of Rodah is another Nilometer, anciently used to show the state of the flood, but whose indications are now too much affected by the drawing off of water in Upper Egypt for irrigation purposes to be reliable. At Cairo the Ismailieh Canal branches off to Ismailia and falls into the Gulf of Suez near the town of Suez. Nineteen miles beyond Cairo is the Barrage, a great bridge whose arches can be closed, converting it into a dam and raising the water level so that the irrigation canals can be supplied. At the Barrage it divides into the Damietta branch, which empties into the Mediterranean at Damietta, and the Rosetta branch, dividing into the Mahmoudieh canal, which has its exit at Alexandria, and the Raschidieh canal, which discharges at Rosetta; a fifth branch anciently flowed through Lake Menzaleh. From these branches the Delta is supplied by numerous smaller canals. Along the north coast are Lakes Mareotis (filled by the British from the sea at the commencement of the century), Edko, Bourlos, etc., which are highly charged with sodium chloride; waters of this description occur also at Shaloof and other places near the Suez Canal (c. f. Richmond and Opp, *J. Soc. Chem. Ind.*, 9, 1108, and Richmond, *Analyst*, 17, 163); the water from these lakes finds its way into the lower branches of the Nile and somewhat alters its character. The waters of the Bahr Yousef are also affected in a similar manner.

## II. THE NILE CHEMICALLY CONSIDERED AS THE WATER SUPPLY OF EGYPT.

The first chemical study was made in 1874-5 by the late Dr. Letheby; he analyzed twelve monthly samples of the water taken at Boulak, sent to him by the Public Works Department; an extract of his analyses is given in Table I; he also made a mineral analysis of each sample.

TABLE I. ANALYSES BY DR. LETHEBY IN 1874-5.

Date.	Height of Nile.	Total solids.	Suspended matter.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	Oxygen absorbed.	Coefficient of purity.
Jan. 23, 1875.....	15.00	14.47	16.74	0.24	0.0087	0.0143	Trace	0.257	67.4
Feb. 12, 1875.....	14.71	14.67	12.57	0.25	0.0048	0.0166	"	0.317	81.0
Mar. 15, 1875.....	14.26	17.81	5.31	0.61	0.0036	0.0086	"	0.417	92.7
Apr. 15, 1875.....	13.24	18.19	6.63	0.92	0.0035	0.0107	"	0.517	104.8
May 13, 1875.....	13.02	20.47	4.77	1.74	0.0014	0.0118	"	0.625	137.1
June 8, 1874.....	12.59	20.30	6.91	1.64	0.0057	0.0114	"	0.300	72.5
July 10, 1874.....	13.76	16.39	17.84	0.85	0.0129	0.0100	"	0.211	54.8
Aug. 12, 1874.....	20.18	16.60	149.16	0.63	0.0043	0.0071	"	0.237	55.4
Sept. 20, 1874.....	22.32	19.44	54.26	0.21	0.0100	0.0171	"	0.386	96.3
Oct. 12, 1874.....	22.83	15.86	37.80	0.49	0.0071	0.0143	"	0.483	112.3
Nov. 12, 1874.....	18.31	14.91	34.37	0.21	0.0064	0.0114	"	0.269	76.5
Dec. 12, 1874.....	16.28	13.61	28.91	0.28	0.0049	0.0108	"	0.186	49.0

In his report to the Public Works Department he drew attention to the variable character of the water, and to the amount of organic matter, and albuminoid ammonia, *which were largely in excess of those in the rivers of Europe*. This last statement laid the foundation for the general opinion that the Nile water is bad, an opinion contrary to that arrived at by the French Expedition at the beginning of the century, who did not, however, make chemical examinations. Wanklyn also examined samples at the same time, and drew attention chiefly to the variation in the chlorine.

The Egyptian chemists Tanquerel 1883, (*Annuaire Egyptienne*, 1891), Pappel, 1886, and Pollard, 1888-9, (*Report of the Sanitary Administration*, 1889) also studied the Nile. Tanquerel did little more than study the mineral constituents; Pappel made twelve monthly analyses (omitting however the determination of suspended matter), but his results are so full of obvious discordances, possibly clerical errors, which a personal reference to this chemist has failed to explain, that they must be rejected

as useless; Pollard made twenty-four bi-monthly analyses of considerable value, which are given in Table II.

TABLE II. ANALYSES BY MR. POLLARD IN 1888-89.

Date.	Height of Nile.	Total solids.	uspended matter.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	Oxygen absorbed.	Coefficient of purity.
Jan. 5, 1889	14.03	13.2	13.6	0.36	...	0.010	0.10	0.32	74.5
" 19, 1889	13.93	14.0	12.8	0.50	0.002	0.010	0.13	0.33	77.0
Feb. 2, 1889	13.69	15.2	10.2	0.71	...	0.009	0.05	0.295	68.2
" 16, 1889	13.52	17.3	8.7	1.14	0.001	0.010	0.04	0.28	66.4
Mar. 2, 1889	13.47	19.5	6.0	0.14	...	0.010	0.04	0.28	66.2
" 16, 1889	13.40	20.2	5.0	1.79	0.001	0.011	0.03	0.32	75.3
Apr. 6, 1889	13.36	23.0	5.9	2.21	...	0.012	0.06	0.29	70.3
" 20, 1889	13.33	25.8	4.0	2.64	...	0.011	0.05	0.27	65.2
May 4, 1889	13.31	26.35	3.2	3.00	0.001	0.011	0.06	0.28	67.5
" 18, 1889	13.33	29.0	1.7	3.43	0.001	0.011	0.08	0.29	69.6
June 8, 1888	13.33	28.3	3.3	4.00	0.002	0.012	0.11	0.27	66.9
" 23, 1888	13.29	23.7	2.27	3.14	0.020	0.037	0.16	0.41	123.8
July 7, 1888	13.36	29.2	1.4	3.00	...	0.020	0.02	0.30	80.1
" 21, 1888	14.14	23.4	6.0	1.93	0.003	0.020	0.03	0.22	64.7
Aug. 4, 1888	14.30	20.3	...	1.50	0.008	0.017	0.03	0.28	74.7
" 20, 1888	17.43	14.3	163.1	0.57	0.005	0.007	0.38	0.30	69.9
Sept. 1, 1888	18.64	13.7	231.2	0.36	0.007	0.010	0.32	0.32	77.0
" 22, 1888	18.55	12.8	163.6	0.29	0.004	0.011	0.19	0.23	58.8
Oct. 6, 1888	17.38	12.2	105.6	0.29	0.003	0.012	0.19	0.205	55.6
" 20, 1888	16.42	12.5	...	0.26	0.001	0.010	0.22	0.22	55.3
Nov. 3, 1888	16.44	13.7	81.3	0.24	...	0.020	0.19	0.25	71.0
" 17, 1888	14.98	12.4	48.3	0.36	0.001	0.007	0.22	0.29	66.3
Dec. 8, 1888	14.39	12.6	26.2	0.29	0.001	0.006	0.17	0.22	51.1
" 22, 1888	14.19	13.6	20.9	0.29	...	0.008	0.11	0.28	64.5

Sundry French chemists have made from time to time analyses too isolated to have any value in the study of a constantly changing River like the Nile.

The whole of the foregoing analyses were made on water taken from the river at Cairo, and no attempt was made to study it at other points.

As already stated the Nile water enjoys a somewhat bad reputation, due in the first instance to Letheby, and greatly enhanced by Pappel, and to some extent Pollard; the grounds for Letheby's opinion have already been stated; Pappel's analyses are unreliable, and therefore his opinion cannot be held to have great weight, though from his position of Chief Government Chemist it was received with authority in Egypt; the latter and Pollard based their opinion on the fact that in the Nile the limits 0.004 parts per hundred thousand of albuminoid ammonia, and 0.2 parts per hundred thousand of oxygen absorbed in the Forehammer process were exceeded. As the Nile is (chemically) almost unknown,

the judging of the water by these arbitrary standards is not entirely defensible; the chemical evidence therefore that the Nile, which has been drunk by generations during six thousand years, is bad for potable purposes, is weak.

At the beginning of 1891 His Excellency, Dr. Greene Pasha, Director of the Sanitary Administration, thought it desirable to examine the water of the Nile as near its source as was possible, and he entrusted the work to my hands; with him I sketched the following plan to include analyses of (a) the Upper Nile at Wady Halfa, Assouan, Keneh, Assiout, Minieh, and Cairo; (b) the Lower Nile at Cairo, Alexandria on the Mahmoudieh canal, Rosetta on the Raschidieh canal, Damietta on the Damietta branch, Ismailia, Port Said and Suez on the Ismailieh canal, and Tantah and Zagazig on two branch canals; (c) the Bahr Yousef, at Assiout, Deyrout, and Medinet-el-Fayoum; (d) at Cairo, to study specially the monthly variations and the water of the Cairo Water Company.

The machinery of the Sanitary Administration was placed at my disposal by His Excellency, Greene Pasha, and through the kindness of Colonel Ross, Chief Inspector of Irrigation, and His Excellency, Rogers Pasha, Principal Medical Officer of the Egyptian Army, I was also able to avail myself of the aid of the Public Works and War departments. I take this opportunity of expressing my thanks to these gentlemen and also to His Excellency, Mahmoud Pasha Sidky, Sub-Director of the Sanitary Administration, to Mohammed Bey Sidky Chief (pro tem.) of the Technical Service Public Works Department, and to the various officials of the three departments who aided me.

All samples, except at Cairo, were taken in mid-stream by plunging a bottle to a distance of half a meter below the surface and there, after rinsing, filling it; the samples at Cairo were taken at the Kasr-el-Nil bridge by myself with the apparatus described hereafter; the water was forwarded with the least possible delay to the Khedivial Laboratory at Cairo, and the analysis immediately commenced.

The analyses are given in Tables III (Cairo), IV (Wady Halfa, Assouan, Keneh, Minieh, and Cairo), V (Alexandria, Rosetta, Damietta, Tantah, and Zagazig), VI (the same and

Cairo) VII (Ismailia, Port Said, Suez, and Cairo), VIII (Assiout, Deyrout, and Medinet-el-Fayoum), IX (Rodah, Kasr-el-Nil, and Embabeh, all near Cairo), and X (showing the effect of filtration through various media). All results are stated in parts per hundred thousand, and were obtained from the water twice filtered through paper to remove suspended matter; this proceeding has some objections, shown in Table X, but as it had been adopted by my predecessors I continued it; all results are, however, comparable (with exceptions mentioned hereafter).

TABLE III. ANALYSES AT CAIRO DURING 1891.

Date.	Height of Nile.	Total solids.	Suspended matter.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
Mar. 25, 1891.....	13.82	17.96	3.84	1.01	0.001	0.025	Trace	0.081	0.186	60.0
Apr. 28, 1891.....	13.98	23.12	4.52	2.09	0.007	0.038	"	0.063	0.160	68.0
May 26, 1891.....	13.82	19.64	1.44	2.91	0.003	0.019	"	0.124	0.264	70.8
June 29, 1891.....	14.23	15.84	6.60	1.41	0.002	0.043	"	0.166	0.289	105.5
July 25, 1891.....	14.48	17.16	31.32	0.64	Trace	0.016	0.03	0.089	0.145	48.2
Aug. 28, 1891.....	18.71	16.20	188.64	0.66	0.002	0.012	0.01	0.084	0.137	42.9
Sept. 31, 1891.....	19.13	13.12	160.44	0.56	0.002	0.008	Trace	0.074	0.124	35.6

TABLE IV. ANALYSES AT CAIRO (CA.), MINIEH (MI.), ASSIOUT (AT.), KENEH (KE.), ASSOUAN (AN.), AND WADY HALFA (W. H.).

Date.	Place.	Total solids.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.	Coefficient of P. corrected.
May.....	Ca.	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8	70.8
".....	Mi.	99.56	39.50	0.004	0.015	2.1	0.119	0.212	...	...
".....	At.	19.96	2.45	0.012	0.039	0.09	0.148	0.267	98.1	98.1
".....	Ke.	21.08	2.00	0.004	0.028	0.08	0.138	0.257	82.5	115.5
".....	An.	...	...	...	...	...	...	...	...	...
".....	W. H.	18.96	1.82	0.001	0.014	Trace	0.063	0.114	38.2	76.4
June.....	Ca.	15.84	1.41	0.002	0.043	"	0.166	0.289	105.5	105.5
".....	Mi.	18.24	1.36	0.006	0.034	0.18	0.097	0.163	71.8	...
".....	At.	14.60	1.32	0.073	0.059	None	0.164	0.372	143.6	143.6
".....	Ke.	14.24	1.14	0.110	0.043	"	0.121	0.248	115.2	161.3
".....	An.	14.64	1.09	0.134	0.031	"	0.104	0.208	99.4	161.0
".....	W. H.	...	...	...	...	...	...	...	...	...
July.....	Ca.	17.16	0.64	Trace	0.016	0.03	0.089	0.145	48.4	48.4
".....	Mi.	18.32	0.86	0.011	0.015	0.25	0.091	0.172	53.8	...
".....	At.	16.36	0.68	Trace	0.010	0.02	0.089	0.145	42.4	42.4
".....	Ke.	15.44	0.64	"	0.017	0.02	0.103	0.187	56.4	79.0
".....	An.	13.84	0.59	"	0.010	Trace	0.094	0.154	43.8	70.1
".....	W. H.	13.20	0.44	"	0.013	"	0.090	0.181	49.1	98.2
August.....	Ca.	16.20	0.66	0.002	0.012	0.01	0.084	0.137	42.9	42.9
".....	Mi.	...	...	...	...	...	...	...	...	...
".....	At.	13.60	0.51	0.005	0.024	Trace	0.075	0.198	60.8	60.8
".....	Ke.	...	...	...	...	...	...	...	...	...
".....	An.	13.20	0.44	Trace	0.013	Trace	0.057	0.139	38.3	61.3
".....	W. H.	11.68	0.32	0.001	0.009	"	0.075	0.159	40.1	80.2

TABLE V. ANALYSES AT ALEXANDRIA, ROSETTA, DAMIETTA, TANTAH, AND ZAGIZIG.

Date.	Place.	Total solids.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
May 17, 1891.	Alexandria.	24.60	2.91	0.004	0.026	0.02	0.112	0.258	75.1
June 19, 1891.	"	24.36	2.68	0.001	0.024	Trace	0.096	0.175	60.9
July 16, 1891.	"	21.04	1.73	0.002	0.018	"	0.072	0.186	46.1
May 20, 1891.	Rosetta.	20.48	2.00	0.012	0.028	0.04	0.128	0.257	81.9
Aug. 20, 1891.	"	...	...	0.001	0.015	Trace	0.062	0.132	40.8
May 15, 1891.	Damietta.	30.36	5.18	0.020	0.040	0.07	0.095	0.161	49.1
June 20, 1891.	"	46.76	11.36	0.006	0.023	Trace	0.069	0.139	36.1
July 16, 1891.	"	30.86	12.86	0.002	0.010	0.09	0.080	0.152	47.4
Aug. 16, 1891.	"	137.68	69.1	0.009	0.014	None	0.112	0.271	73.3
May 24, 1891.	Tantah.	22.73	2.77	0.009	0.022	"	0.112	0.271	73.3
July 12, 1891.	"	17.32	1.23	0.001	0.013	0.06	0.067	0.137	40.6
June 10, 1891.	Zagazig.	23.96	2.64	0.010	0.013	Trace	0.064	0.109	38.7
July 14, 1891.	"	17.84	1.14	0.001	0.020	0.05	0.065	0.133	46.7
Aug. 10, 1891.	"	16.88	0.87	0.001	0.010	0.02	0.062	0.134	36.1

TABLE VI. AVERAGES OF TABLE V.  
(Difference in total solids, corrected for chlorine.)

Place.	Total solids.	Chlorine.	Coefficient of purity.
Cairo .....	18.94	1.51	73.1
Alexandria .....	23.33	2.44	60.8
Difference .....	+2.84	+0.93	-12.3
Cairo .....	18.39	1.34	67.1
Damietta .....	63.90	24.62	58.9
Difference .....	+6.71	+23.28	-8.2
Cairo .....	18.39	1.34	67.1
Tantah .....	20.02	2.00	55.9
Difference .....	+0.53	+0.66	-12.2
Cairo .....	17.21	1.65	60.8
Zagazig .....	19.55	1.55	40.5
Difference .....	+2.50	-0.10	-20.3

TABLE VII. ANALYSES AT CAIRO, ISMAILIA, PORT SAID, AND SUEZ.

Date.	Place.	Total solids.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
April-May .....	Cairo.	23.12	2.09	0.007	0.038	Trace	0.063	0.160	68.0
" " .....	Ismailia.	25.50	2.82	0.009	0.024	0.05	0.121	0.274	77.5
May-June .....	Cairo.	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8
" " .....	Ismailia.	19.96	2.77	0.002	0.024	0.18	0.099	0.236	68.7
" " .....	Suez.	24.60	3.86	0.003	0.019	Trace	0.098	0.236	62.8
" " .....	Port Said.	22.82	2.86	Trace	0.013	"	0.054	0.137	37.5
June-July .....	Cairo.	15.84	1.41	0.002	0.043	"	0.166	0.289	105.5
" " .....	Ismailia.	16.56	1.36	0.004	0.029	0.04	0.108	0.204	72.0
" " .....	Suez.	27.00	4.07	0.001	0.022	Trace	0.091	0.174	57.8
" " .....	Port Said.	20.52	2.27	0.001	0.013	"	0.053	0.106	34.4
July-August....	Cairo.	17.16	0.64	Trace	0.016	0.03	0.089	0.145	45.2
" " .....	Ismailia.	16.08	0.67	0.003	0.021	0.07	0.079	0.145	52.2
" " .....	Suez.	22.36	3.03	0.001	0.017	Trace	0.091	0.168	52.2
" " .....	Port Said.	16.84	1.01	Trace	0.012	"	0.065	0.124	37.4

TABLE VIII. ANALYSES AT ASSIOUT, DEYROUT, AND MEDINET-EL-FAYOUM.

Date.	Place.	Total solids.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
May .....	Assiout.	19.96	2.45	0.012	0.039	0.09	0.148	0.267	98.1
" .....	Deyrout.	17.40	...	0.006	0.027	0.04	0.114	0.250	76.2
" .....	Fayoum.	47.32	11.73	0.002	0.037	0.01	0.110	0.226	70.0
June .....	Assiout.	14.60	1.32	0.073	0.059	None	0.164	0.372	143.6
" .....	Deyrout.	15.28	1.26	0.001	0.038	0.17	0.111	0.214	82.6
" .....	Fayoum.	49.28	13.00	0.002	0.025	Trace	0.086	0.135	55.9
July .....	Assiout.	16.36	0.68	Trace	0.010	0.02	0.089	0.145	44.4
" .....	Deyrout.	17.00	0.82	0.008	0.023	0.26	0.079	0.160	57.7
" .....	Fayoum.	27.56	4.48	0.001	0.037	0.03	0.119	0.248	85.9

Mean coefficient of purity :

Assiout ..... 93.7

Deyrout ..... 72.2

Fayoum ..... 70.3

TABLE IX. ANALYSES AT RODAH, KASR-EL-NIL, AND AFTER KEEPING.

Place.	Total solids.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.
Rodah .....	20.08	2.82	0.002	0.019	0.01	0.112	0.256	67.4
Kasr-el-Nil.....	19.64	2.91	0.003	0.019	Trace	0.124	0.264	70.8
Embahah .....	19.72	2.82	0.004	0.018	0.01	0.129	0.275	72.1
Embahah after 6 weeks	...	...	0.002	0.013	0.13	0.051	0.108	34.9

TABLE X. SHOWING THE EFFECT OF FILTRATION THROUGH VARIOUS MEDIA.

Designation.	Ammonia.		Nitric acid.	O absorbed.		Coefficient of purity.
	Free.	Albuminoid.		15 min.	4 hrs.	
a .....	0.010	0.021	Trace	0.127	0.200	68.4
b .....	Trace	0.016	0.03	0.089	0.145	48.4
c .....	Trace	0.009	0.13	0.057	0.080	29.0
d .....	0.014	0.005	None	0.017	0.030	14.2

[TO BE CONTINUED.]

## ANNOUNCEMENT OF THE JOINT COMMITTEE ON THE WORLD'S FAIR CHEMICAL CONGRESS.

### TO AMERICAN CHEMISTS.

The World's Congress Auxiliary and the American Chemical Society have united in calling a meeting of the chemists of the world to attend a general Chemical Congress to be held in Chicago, beginning August 21st, 1893.

The members of the committee on the part of the World's Congress Auxiliary are Professors J. H. Long, W. S. Haines, M. Delafontaine, A. V. E. Young, and W. L. Brown, all of Chicago.

The members on the committee on the part of the American Chemical Society are Dr. Wm. McMurtrie, of 106 Wall street, New York; Professor C. F. Chandler, Columbia College, New York; Professor A. B. Prescott, Ann Arbor, Michigan; Professor C. E. Munroe, Washington, D. C., and Dr. H. W. Wiley, of Washington, D. C.

The two committees have organized by selecting H. W. Wiley as Chairman and R. B. Warder, of Washington, D. C., as Secretary. The committee has appointed as the Advisory Council of the World's Congress of Chemists, a number of distinguished American and foreign gentlemen.

The American chemists who have been selected to act on this Advisory Committee are as follows:

P. T. Austen, New York.	F. A. Gooch, New Haven.
S. M. Babcock, Madison.	E. Hart, Easton.
E. H. S. Bailey, Lawrence.	J. B. Herreshoff, New York.
G. F. Barker, Philadelphia.	E. W. Hilgard, Berkeley.
H. C. Bolton, New York.	H. B. Hill, Cambridge.
H. Bower, Philadelphia.	C. L. Jackson, Cambridge.
A. A. Breneman, New York.	S. W. Johnson, New Haven.
G. C. Caldwell, Ithaca.	E. H. Keiser, Bryn Mawr.
R. H. Chittenden, New Haven.	J. W. Langley, Cleveland.
F. W. Clarke, Washington.	M. C. Lea, Philadelphia.
J. P. Cooke, Cambridge.	A. R. Leeds, Hoboken.
H. B. Cornwall, Princeton.	H. Leffmann, Philadelphia.
T. M. Drown, Boston.	M. Loeb, New York.
C. B. Dudley, Altoona.	J. W. Mallet, University of Virginia.
W. L. Dudley, Nashville.	A. Michael, Bonchurch.
P. C. Freer, Ann Arbor.	E. W. Morley, Cleveland.
W. Gibbs, Newport.	H. N. Morse, Baltimore.
C. A. Goessman, Amherst.	J. U. Nef, Chicago.



H. H. Nicholson, Lincoln.  
 T. H. Norton, Cincinnati.  
 W. A. Noyes, Terre Haute.  
 J. M. Ordway, New Orleans.  
 W. R. Orndorff, Ithaca.  
 I. Remsen, Baltimore.  
 A. H. Sabin, New York.  
 S. P. Sadtler, Philadelphia.

E. F. Smith, Philadelphia.  
 E. R. Squibb, Brooklyn.  
 W. E. Stone, Lafayette.  
 V. C. Vaughan, Ann Arbor.  
 R. B. Warder, Washington.  
 E. S. Wood, Boston.  
 T. H. Wormley, Philadelphia.

The foreign chemists who have been asked to serve on this committee are the following:

Sir F. A. Abel, London.  
 P. Alexejew, Kiew.  
 W. Alexejew, St. Petersburg.  
 A. H. Allen, Sheffield.  
 H. E. Armstrong, London.  
 A. Arnaud, Paris.  
 S. Arrhenius, Stockholm.  
 G. Arth, Nancy.  
 A. v. Baeyer, Munich.  
 L. Balbino, Messina.  
 P. Barbier, Lyons.  
 H. Baubigny, Paris.  
 E. Baumann, Freiburg.  
 A. Bechamp, Paris.  
 H. Becquerel, Paris.  
 P. P. Bedson, Newcastle.  
 F. Beilstein, St. Petersburg.  
 Sir L. Bell, Rounton Grange.  
 R. Benedikt, Vienna.  
 A. Bernthsen, Mannheim.  
 M. P. Berthelot, Paris.  
 R. Biedermann, Berlin.  
 C. A. Bischoff, Riga.  
 C. W. Blomstrand, Lund.  
 L. de Boisbaudran, Paris.  
 B. Brauner, Prague.  
 L. Brieger, Berlin.  
 A. C. Brown, Edinburgh.  
 J. C. Brown, Liverpool.  
 J. W. Brühl, Heidelberg.  
 H. Brunner, Liverpool.  
 G. Bunge, Basel.  
 A. Cahours, Paris.  
 S. Cannizzaro, Rome.  
 A. M. Chance, Oldbury.  
 H. Le Chatelier, Paris.  
 G. Ciamician, Bologna.  
 A. Classen, Aachen.  
 A. Claus, Freiburg.  
 P. T. Cleve, Upsala.  
 F. Clowes, Nottingham.  
 J. N. Collie, London.  
 W. Crookes, London.  
 Th. Curtius, Kiel.

O. Dammer, Berlin.  
 P. P. Deherain, Paris.  
 J. Dewar, Cambridge.  
 H. B. Dixon, Manchester.  
 G. Dragendorff, Dorpat.  
 E. Drechsel, Bern.  
 E. Duclaux, Paris.  
 E. Erlenmeyer, Aschaffenburg.  
 A. Etard, Paris.  
 E. Fischer, Berlin.  
 F. Fischer, Göttingen.  
 F. Fittica, Marburg.  
 R. Fittig, Strassburg.  
 E. Frankland, Reigate.  
 P. F. Frankland, Dundee.  
 E. Frémy, Paris.  
 R. Fresenius, Wiesbaden.  
 Ch. Friedel, Paris.  
 C. Gaechtens, Giessen.  
 A. Gamgee, Manchester.  
 A. Gautier, Paris.  
 D. Gernez, Paris.  
 A. Girard, Paris.  
 J. H. Gladstone, London.  
 C. Graebe, Geneva.  
 E. Grimaux, Paris.  
 C. E. Groves, London.  
 C. M. Guldberg, Christiana.  
 W. D. Halliburton, London.  
 O. Hammarsten, Upsala.  
 M. Hauriot, Paris.  
 A. R. Hantzsch, Zurich.  
 J. Hargreaves, Widnes.  
 A. V. Harcourt, Oxford.  
 W. N. Hartley, Dublin.  
 R. Hasenclever, Aachen.  
 O. Hehner, London.  
 W. Hempel, Dresden.  
 E. Herter, Berlin.  
 J. H. van't Hoff, Amsterdam.  
 F. Hofmeister, Prague.  
 F. Hopp-Seyler, Strassburg.  
 A. Horstmann, Heidelberg.  
 D. Howard Walthamstowe.

C. G. Hüfner, Tübingen	W. H. Perkin, Sudbury.
J. J. Hummel, Leeds.	W. H. Perkin, Jr., Manchester.
H. Huppert, Prague,	A. Petermann, Gembloux.
F. Hurter, Widnes.	M. v. Pettenkofer, Munich.
M. Jaffé, Königsberg.	S. U. Pickering, Herts.
E. Jungfleisch, Paris.	A. Pinner, Berlin.
A. Kekulé, Bonn.	J. Post, Hannover.
S. H. B. Kerl, Berlin.	H. R. Proctor, Leeds.
A. Kossel, Berlin.	W. Ramsay, London.
G. Krause, Cöthen.	F. M. Raoult, Grenoble.
G. Krüss, Munich.	B. Redwood, London.
A. Ladenburg, Breslau.	J. E. Reynolds, Dublin.
H. Landolt, Berlin.	C. H. L. Ritthausen, Königsberg.
Ch. Lauth, Paris.	Sir H. E. Roscoe, London.
J. B. Lawes, Rothamstead.	P. Sabatier, Toulouse.
J. A. Le Bel, Paris.	K. Salkowski, Berlin.
J. Lemberg, Dorpat.	O. L. Salomon, Berlin.
I. Levinstein, Manchester.	W. Saunders, Ottawa.
A. Lieben, Vienna.	C. Scheibler, Berlin.
O. Liebreich, Berlin.	A. Scheuerer-Kestner, Charron.
H. Limpricht, Greifswald.	H. Schiff, Florence.
C. Lintner, Munich.	T. Schloesing, Paris.
A. Liversidge, Sidney.	O. Schmiedeberg, Strassburg.
W. Lossen, Königsberg.	T. Schneider, Paris.
E. Ludwig, Vienna.	P. Schützenberger, Paris.
G. Lunge, Zurich.	E. Schunck, Kersal.
M. Maerker, Halle.	H. Schwanert, Greifswald.
R. Meldola, London.	F. Selmi, Bologna.
D. Mendeleëff, St. Petersburg.	K. Seubert, Tübingen.
E. v. Meyer, Leipsic.	W. Smith, London.
L. Meyer, Tübingen.	A. Smithells, Leeds.
V. Meyer, Heidelberg.	F. Sohxlet, Munich.
K. A. Moerner, Stockholm.	W. Spring, Lüttich.
L. Mond, London.	W. Staedel, Darmstadt.
G. Monselise, Milan.	F. Stohmann, Leipsic.
H. F. Morley, London.	A. Stutzer, Bonn.
A. Mosso, Turin.	F. Sutton, Norwich.
M. M. P. Muir, Cambridge.	J. Thomsen, Copenhagen.
A. Muntz, Paris.	T. E. Thorpe, London.
E. K. Muspratt, Liverpool.	F. Tiemann, Berlin.
A. Naumann, Giessen.	W. A. Tilden, Birmingham.
M. Nencki, St. Petersburg.	G. Tschermak, Vienna.
W. Nernst, Leipsic.	P. Waage, Christiania.
B. E. R. Newlands, London.	R. Warrington, Harpenden.
R. Nietski, Basel.	A. C. Williams, Sheffield.
L. F. Nilson, Stockholm.	A. W. Williamson, London.
E. Noelting, Mulhouse.	H. Willm, Lisle.
W. Odling, Oxford.	C. Winkler, Freiberg.
W. Ostwald, Leipsic.	J. Wislicenus, Leipsic.
C. O'Sullivan, Burton-on-Trent.	C. R. A. Wright, London.
H. Pellet, pres Huy, Belgium.	G. Wyruboff, Paris.

A preliminary organization of the Congress has been made by the committee by dividing the subjects to be discussed into ten classes, namely: Agricultural Chemistry, Analytical Chem-

istry, Didactic Chemistry, Historical Chemistry and Bibliography, Inorganic Chemistry, Organic Chemistry, Physical Chemistry, Physiological Chemistry, Sanitary Chemistry, and Technical Chemistry.

The Committee selected as temporary Chairmen of these sections for the purpose of organization the following named gentlemen, who have accepted the positions and commenced work thereon: Agricultural Chemistry, H. W. Wiley; Analytical Chemistry, Professor A. B. Prescott, Ann Arbor, Michigan; Didactic Chemistry, Professor W. E. Stone, La Fayette, Indiana; Historical Chemistry and Bibliography, Dr. H. C. Bolton, University Club, New York; Inorganic Chemistry, F. W. Clarke, Geological Survey, Washington, D. C.; Organic Chemistry, Professor Ira Remsen, Johns Hopkins University, Baltimore, Maryland; Physical Chemistry, Professor R. B. Warder, Howard University, Washington, D. C.; Physiological Chemistry, Professor V. C. Vaughan, Ann Arbor, Michigan; Sanitary Chemistry, Dr. H. Leffmann, 715 Walnut street, Philadelphia, Pennsylvania; and Technical Chemistry, Dr. Wm. McMurtrie, 106 Wall street, New York.

A circular stating the purpose of the Congress has been sent to all foreign chemists whose names and addresses could be obtained. A second circular is in preparation, giving more detailed accounts of the character of the meeting, the organization of the committees, and other matters relating to the Congress and this will be sent in a few days to all chemists whose addresses can be secured. A third circular will probably be issued later, showing as far as possible the program which will be followed, with the titles of the papers which will be read, and other matters relating to the organization of the Congress.

Quarters for the Congress will be provided by the World's Columbian Exposition authorities and it is expected that the Congress will continue in session from ten days to two weeks.

An especial effort has been made to enlist the co-operation of distinguished foreign chemists. Each chairman of a subsection has submitted the names of those whom he wishes to be particularly invited to deliver addresses or read papers before the Congress to the Chairman of the Joint Committee, who has

in each case sent an invitation on behalf of the committee. Nearly three hundred invitations of this kind have been sent to distinguished foreign chemists and many acceptances have already been received.

It is the intention to have the papers divided in such a way that those of a more popular character will be delivered as addresses before the whole congress, while those of a more strictly scientific character will be read in meetings of the several subsections. Provision will be made for the publication of the proceedings of the Congress in a volume, which can be secured by all members of the Congress who wish to have it. It is expected that the discussion of the papers will take a wide range and that all the problems which are now occupying the minds of the world's chemists will receive due consideration. The language of the Congress will be either, English, French, or German, as the speaker may elect, but it is thought that most of the papers and addresses will be given in English. Several foreign chemists who have accepted invitations to read papers have sent word that they would read in English.

It is hoped that all American chemists will take a special interest in this Congress. It is due to the distinguished visitors who shall come to our shores at that time, that they receive proper attention from their co-laborers on this side of the water. Through the American Chemical Society the chemists of the United States are securing a powerful organization, and it is to the members of this Society that this appeal is especially made to be present and take part in the proceedings of the Congress. But the co-operation of all American chemists is earnestly desired. Not only is this a scientific, but a patriotic duty and every chemist in the United States should feel that it is his privilege as well as duty to do something towards making the Congress a success. The best thing he can do of course, is to be present at its meetings and take part in its proceedings, and it is hoped that the great majority of the members of the American Chemical Society may find it possible to arrange their business affairs so as to be present in Chicago from the 15th to the 31st of August.

During this time other meetings of interest to chemists will

take place in or near Chicago. The American Association will hold its meeting in the latter part of August, at Madison, Wisconsin, and the Chemical Section is one of the most powerful sections of that Association. It is probable that the next meeting of the Association of Official Agricultural Chemists will be held in Chicago at or near the time of the World's Congress. The American Pharmacists' Association will also hold its annual meeting in Chicago at about this time and there is a very strong chemical section in this Association. It is thought also that the Mining Engineers may hold a meeting in Chicago, at about this date, although this is a matter which is not yet definitely determined.

When all these facts are considered it is seen that the opportunity is now offered American Chemists of promoting one of the most important Congresses that the science of chemistry has ever called together; a Congress which will not only be of absorbing interest during its meetings, but far reaching in its influence on the science and practice of chemistry in all parts of the world.

For particulars in regard to the place and time of meeting, and for information concerning the obtaining of quarters, and for all detailed matters concerning the Congress, American chemists are requested to address Professor J. H. Long, corner 26th street and Prairie avenue, Chicago, Ill., who will turn the requests over to the proper Committee for attention. Titles of papers to be presented should be sent to the Chairmen of the several subsections, or to the Chairman of the Joint Committee.

H. W. WILEY,  
Chairman of the Joint Committee.

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### PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, etc.*—Orrin B. Peck has a number of patents on a centrifugal ore separator (489,090, 489,197 to 489,205 and 490,084), and 490,041, a centrifugal amalgamator. Nos. 489,744, 490,849, and 490,850 were granted George Johnston for an ore concentrator; 490,911 to Wilhelm Krug for an ore

separator; 489,538 to William S. Lockhart and E. W. Streeter for a hydraulic mineral separating apparatus; 489,797 to Charles Faber for an ore washing machine; and 489,101 to Charles E. Seymour for an ore separator. Horace F. Brown has two patents on an ore roasting furnace (489,142-143). John E. Chaster (492,711), Fred O. Norton (491,686), and Charles C. Ormsby (492,425) have each patented an ore amalgamator, while the last also covers his process by 492,426. Orrin B. Peck has a "machine for centrifugally treating molten materials" (491,131), and Adolph Schulenberg an ore crushing mortar (492,634). William H. Howard invents an apparatus for removing matte from slags (489,307).

*Iron and Steel.*—Walter E. Koch has patented a new furnace for heating steel ingots (489,017). 490,451 is a method for making metal plates by John B. Nau, and 490,236 a process for manufacturing sheet iron by Walter D. Wood. John B. Jenkins heats malleable cast iron, cast steel, Bessemer steel, etc., in contact with a compound consisting of granulated or powdered charcoal, manganese dioxide, chloride of sodium, cyanide of potassium, and chloride of ammonium, as a new process for the manufacture of steel (490,660). Another process (491,035), Taylor Allderdice, inventor, consists in placing a sufficient quantity of free carbon in a ladle to raise the carbon content of the steel to the point desired, and then pouring the metal into the ladle from the converter. Antoine P. G. Rollet is the inventor of a process for purifying pig iron, which consists in mixing the iron with fuel, limestone, fluor-spar, and iron oxide, subjecting the mixture to the action of a blast and separating the refined iron (491,498) while 491,508 is the patent on the cupola furnace in which the operation is carried on. To convert malleable iron into steel, A. J. Hindermeyer uses plumbago, salt, and sulphuric acid (492,679). Alfred E. Hunt manufactures steel in the following way (493,090): The iron is first refined, and to it a deoxidizing agent is added; then the refined metal is recarburized by the addition of free carbon in sticks in definite proportions. A furnace for "roasting, calcining, and oxidizing metals and their compounds," invented by Herman Frasch, is protected by 492,551, and 491,274 is granted Thomas

Thomas for a desulphurizing furnace. A. Crossley has also a furnace for producing ferro-ferric and ferric oxides (491,085).

*Nickel*.—Numbers 489,574-575-576 and 881 are patents for obtaining and separating sulphide of nickel granted to Robert M. Thompson. The crude nickel obtained by smelting the ore with a suitable flux is resmelted with niter or salt cake with an excess of carbon, the sodium sulphide formed uniting with the nickel to form nickel sulphide, which is separated by specific gravity. John L. Thomson (489,882) uses instead of niter or salt cake in presence of carbon, sulphides of any of the alkaline metals or ammonium to produce sulphide of nickel. Arthur S. Grant, *et al.* (490,847) fuses ores containing nickel with calcium sulphate or other sulphates and the less easily oxidizable metals, as nickel, are left as sulphides.

*Lead*.—John J. Crooke frees copper and lead from foreign metals by fusing, then heating in an air blast to form oxides, and while fused, adding ammonium chloride and finely divided carbon (491,084). Andrew Honman and Victor Vulliez, of Victoria, protect their process, in this country, for the manufacture of white lead by U. S. patent 489,254. The reduced galena is roasted, treated with neutral lead acetate, the basic lead acetate formed is conveyed to a settling tank, then discharged into a closed vat, and the solution is subjected to the action of carbonic acid to precipitate the white lead. Norman K. Morris and John W. Bailey manufacture white lead by two processes. The first (493,173) consists in pulverizing lead carbonate and hydrated lead oxide and mixing with a volatile oil of the petroleum type; 493,106, the second, is described as first forming lead fiber into independent masses, charging with acetic acid by dipping and then exposing to the action of carbon dioxide and aqueous vapor. Bernhard Rösing (494,349) brings a molten oxygen compound of lead, as litharge, in contact with a sulphide, as galena, in order to separate the metal. Carl V. Petraeus (492,832) smelts lead ores in a low cupola furnace; pulverized galena in admixture with air is injected into the upper part of the furnace, and the resultant fumes are screened, making a lead pigment. Paul Bronner (491,635) digests crude lead sulphate with sulphuric acid, washes, treats with sodium

carbonate, washes, dries and heats in a muffle the carbonate of lead thus obtained, digests the pure oxide of lead with lead acetate and precipitates with carbon dioxide to produce white lead. Horace F. Brown has a patent furnace for condensing lead fumes (489,144).

*Tin.*—Camille L. C. Bertou proposes (489,624) a process for precipitating oxide of tin from solutions, which consists in precipitating the tin from solutions containing it by carbonate of lime, adding the precipitant while the solution is exposed to the air at a temperature just below boiling, then cooling the liquid after complete precipitation, washing the precipitate with cold water and then suspending it in a solution of an alkaline carbonate, the strength of which is gradually increased until it has a faintly alkaline reaction. To separate tin from iron and steel Thomas Twynam first coats the surface of the tin with a special preparation, then oxidizes the metal and separates it from the iron (491,254).

*Carbonic Acid.*—For the preparation of pure carbon dioxide. E. Luhmann leads gases containing carbonic acid into sodium phosphate and heats to liberate the carbon dioxide (491,365).

*Alkali Recovery and Ammonium Chloride.*—Henry C. Higginson describes a new apparatus for the manufacture of whiting (491,353), and Godfrey L. Cabot (491,923) has an improved process for producing lamp black. Henry Blackman (492,382) describes an apparatus for recovering alkali, and Ludwig Mond (491,741) has an original form of apparatus for volatilizing ammonium chloride, zinc chloride and antimony being filled into the bottom of the retort which is exposed to the direct flame, while the ammonium chloride is fed from above through a hopper.

*Manganese.*—Professor Green and Dr. Wahl have a patent process for manufacturing manganese and its alloys, free from carbon (489,303). The ore is digested with dilute sulphuric acid, then the manganese in solution is reduced first to manganous oxide, then to the metallic state by heating in a furnace free from carbon, in contact with the chemically equivalent quantity of a metal capable of removing its oxygen.

*Aluminum.*—Thomas L. Wilson has two patents. 491,394 is



on a process for electrically reducing aluminum and forming alloys from the metal. Alumina is electrolyzed, the anode consisting of molten base metal and the cathode of carbon, in the presence of finely divided carbon, the reduced aluminum uniting with the base metal to form an alloy. In connection with aluminum, we may mention a composition for soldering the metal which Georg Wegner proposes (490,840), *viz.*, 165 parts lead, 100 parts tin, and nine parts zinc, and his process for electroplating aluminum (490,841), which is as follows: The metal is first dipped into a bath at boiling temperature containing cyanides of silver and mercury to heighten its activity, then electrically coated with zinc, in a bath containing chloride of zinc and sulphate of soda, to protect the aluminum against the acid bath in coppering, silvering, gilding, etc.

*Gold and Silver.*—W. P. Miller patents a process for recovering precious metals (492,040) which is mechanical in its application; while John Blair places gold ores, saturated with a solution of sodium chloride and nitrate, in a perforated vessel, in a solution of sulphuric acid, and the soluble parts are washed back into the acid (492,133). Carl Moldenhauer treats ores bearing gold with a solution of potassium cyanide in the presence of potassium ferri-cyanide (492,221). Samuel H. Cochran also patents a process for separating the noble from the base metals (491,638). Frederick P. Dewey treats mixtures containing sulphides of silver and copper with concentrated sulphuric acid, then adds water, precipitates the silver by copper, and recovers the sulphate of copper from the remaining solution (490,068). William B. Jackson patents his process for treating ores (490,659), the steps in which are first chlorination of the ores, then solution of the chlorides in hyposulphite, and finally precipitation of the metals by the action of one or more zinc plates. To obtain gold, silver, and copper from their ores, Andrew French (490,193) mixes the pulverized ores with small percentages of niter cake or sodium bisulphate and common salt, treats in a furnace at a red heat, then leaches the mass.

*Zinc.*—489,460-461 are two patents granted to Parker C. Choate, for a process for obtaining metallic zinc. An ore of zinc carrying lead is heated with a reducing agent in a furnace,

to which air is admitted, so as to volatilize the lead and zinc and other volatile constituents, heating the mixed lead and zinc fumes to "volatilize those constituents more volatile than zinc, and to granulate and condense the mass." The zinc is then reduced with carbon and distilled, and the molten lead is drawn off. Robert F. Nenninger produces zinc oxide from the sulphate of sulphite of zinc (489,873) by precipitating the solutions with lime, boiling the collected precipitate with a concentrated solution of zinc sulphate, and after filtering the solution, the filtrate is evaporated to dryness and leached with water.

*Metallic Alloys.*—Prof. William H. Greene and Dr. Wahl have received a patent (490,961) for their process for producing metallic alloys. In brief, a metallic oxide is heated with a silicide of a metal capable of uniting with the reduced metal, in a furnace in the presence of suitable fluxes. A metallic alloy, consisting of pig iron, ferro-manganese, chromium, tungsten, aluminum, nickel, copper, and bar iron, is claimed by Frederick W. Martino (489,314) for the manufacture of tools and other purposes, and Frank G. Stark (490,174) makes an alloy consisting of fifty-six parts copper, forty parts zinc, two parts iron, and one part aluminum. To coat metals (491,220) William Mild dips the metal first in warm dilute sulphuric acid, next rinses in cold water, then immerses in a bath containing 200 pounds hydrochloric acid, two pounds ammonium chloride, ten pounds zinc spelter, and dries. The bath used for finally coating the metal contains the following proportions per ton: 1,300 pounds lead, 700 pounds block tin, half pound bismuth, six ounces sodium, and two pounds of ammonium chloride, and the solution in which the article to be coated is finally dipped contains one pound of ammonium chloride in forty gallons of boiling water. Frank M. Harris amalgamates a metal, and unites the amalgam to an "amalgamable metallic base" and by expelling the mercury thus unites the two metals (489,077). 492,377 is an electrical process for reducing refractory metallic ores. "Production of Artificial Crystalline Carbonaceous Materials" is the high-sounding name given to a method for preparing silicide of carbon, Edward G. Acheson, patentee (492,767); substances containing carbon, silicon, free or com-

bined, and a chloride of an alkali metal are subjected to the electric current.

*Electrolysis.*—C. J. Theuerner (490,816) subjects silver coated with oxide to an electrolytic bath containing prussiate and cyanide of potash, the oxide-coated silver being suspended as the anode, for the purpose of cleaning the silver. Emile Denorus (491,799) has a novel solution for electroplating, consisting of snail albumen and silver nitrate, in which the article to be coated is first dipped. 489,632 applies to regenerating or cleaning electrolytic solutions by freeing from arsenic by mixing them with metastannic acid, heating until a combination is effected between the arsenic and metastannic acid, and the salt formed is precipitated. The metastannic acid is then recovered (489,633) by dissolving the compound in concentrated hot sulphuric acid, adding an oxidizing agent, and then diluting the mixture until free metastannic acid is precipitated.

*Pottery-ware.*—William M. Brewer (491,074) burns clay, then grinds it to powder and mixes with it one-third its bulk of raw or unburnt clay, and finally adds glass, sand, flint, slaked lime, and common salt, when it is stored away and tempered for use in making pottery-ware.

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#### NOTES.

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Professor Lewis Mills Norton, of the Massachusetts Institute of Technology, and a member of the Council of the American Chemical Society, died April 26, of pneumonia. Professor Norton was born at Athol, Mass., and was educated at the Massachusetts Institute of Technology, where he graduated in 1875. He studied abroad at Giessen, Germany, and returning, was made an Instructor in Sanitary Chemistry and Qualitative Analysis. Soon afterwards he became Assistant Professor of Organic Chemistry, and in 1885 Associate Professor of Industrial Chemistry.

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A committee has been organized for the purpose of erecting a monument to Jean Servais Stas and publishing an edition of his works. The American members are Messrs. F. W. Clarke,

Washington, D. C., J. Hall, Albany, N. Y., and J. W. Mallett, University of Virginia, Va.

A committee, with Professor Sir H. Roscoe as president, solicits subscriptions to a memorial to the late Professor C. Schorlemmer. This is to take the form of a Laboratory of Organic Chemistry at the Owens College, Manchester, to be called the "Schorlemmer Laboratory." Subscriptions may be sent to G. H. Bailey, Secretary, The Owens College, Manchester. £5,000 will be required, of which more than £1,000 had been subscribed before the circular was issued. Adolf Spiegel contributes a biography of Schorlemmer to the index number of the *Berichte der deutschen chemischen Gesellschaft* for 1892.

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## PROCEEDINGS.

### MINUTES OF THE COUNCIL OF THE AMERICAN CHEMICAL SOCIETY, 1893.

JANUARY 9, 1893.

Lewis M. Norton, of Boston, Mass., was chosen a member of the council for the year 1893, to fill the vacancy caused by the election of H. W. Wiley to the presidency of the society.

The following named persons were elected members of the society:

Allen, Walter S., Boston, Mass.  
Bruckmann, G. T., Brooklyn, N. Y.  
Du Pont, Pierre S., Wilmington, Del.  
Heerlein, Robert, Natrona, Pa.  
Leffmann, Dr. H., Philadelphia, Pa.  
Osborne, Thomas B., New Haven, Conn.  
Platt, Charles, Buffalo, N. Y.  
Mertens, Cyril P., Newark, N. J., was elected an associate.

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JANUARY 11, 1893.

The following persons were elected as the standing committee on Nominations to Membership for the year 1893: C. A. Doremus, William McMurtrie, H. C. Bolton.

The following named persons were chosen as the Finance Committee for the year 1893: A. P. Hallock, J. H. Stebbins, Jr., Durand Woodman.

The following were adopted as by-laws for the society:

The president and the general secretary of the society shall be respectively president and secretary of the council.

The annual dues for members and associates shall be five dollars (\$5).

Any member or associate in arrears for dues for three months shall not thereafter receive the journal of the society until all his arrears are paid.

Any person in arrears for dues for one year shall cease to be a member or associate of the society until all his arrears are paid, when he shall be reinstated as a member or associate, unless a valid objection to such reinstatement be made in writing by a majority of the members of the council.

The treasurer shall give written notice to the editor, of all persons in arrears for three months and to the general secretary, of all those in arrears for one year, in order that the editor and the general secretary may carry into effect the provisions of the by-laws regarding such cases. He shall also give similar written notice whenever such arrears are fully paid.

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JANUARY 14, 1893.

J. H. Stebbins, Jr., declined his election as member of the Finance Committee.

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FEBRUARY 10, 1893.

The following named persons were elected as members of the society:

Atwater, Richard M., Syracuse, N. Y.  
 Atwater, Christopher G., Pittsburg, Pa.  
 Bloomfield, L. M., Columbus, O.  
 Drown, T. M., Boston, Mass.  
 Elliott, Russell, Rochester, N. Y.  
 Hebden, John C., Providence, R. I.  
 Hedrick, William A., Washington, D. C.  
 Kemoe, Isaac, Buffalo, N. Y.  
 Lyon, T. L., Lincoln, Neb.  
 Neiman, Howard S., Albany, N. Y.  
 Newman, Herman E., Cincinnati, O.  
 Nickel, Herman L., Cincinnati, O.  
 Palmer, Arthur W., Champaign, Ill.  
 Parr, Samuel M., Champaign, Ill.  
 Peek, Robert Lee, New York, N. Y.  
 Ramsey, A. C., Cincinnati, O.  
 Smith, Irwin J., Cincinnati, O.  
 Tucker, G. P., Washington, D. C.  
 Warder, Robert B., Washington, D. C.  
 Whitehead, Cabell, Washington, D. C.

The following named were elected associates:

Boykin, B. M., Washington, D. C.  
 Phelps, C. Preston, Washington, D. C.  
 Randall, W. B., Washington, D. C.  
 Schneider, O. J., Washington, D. C.

FEBRUARY 15, 1893.

Edgar F. Smith, of Philadelphia, Pa., was elected a member of the Standing Committee on Papers and Publications for the year 1893.

The following were adopted as by-laws for the society:

Each local section shall transmit to the general secretary of the society the names of all its officers and standing committees within three weeks of the date of their election or appointment; and in like manner shall notify the general secretary of any change of officers or standing committees during the year.

So far as practicable, each local section shall report to the general secretary, at least once each year, a prospectus of its plan of work, proposed meetings, etc.

On or before the fifteenth day of November in each year, each local section shall transmit to the general secretary its annual report to the society. This report shall include an outline of the work done by said local section during the year ending October 31, a statement of the meetings held by the section, papers read, subjects discussed, etc.; also, the names of all the officers and standing committees of the section at the date of the report, a statement of the net increase or decrease in its membership; and also, any other items of special interest.

No person shall become a member of any local section, who is not a member of the American Chemical Society.

All papers presented at any local section shall be considered as presented to the society, and may, at the discretion of the Committee on Papers and Publications, be printed in the journal of the society, or published in some other form; also, the proceedings of any local section, in so far as they may be of general interest to the society, may at the discretion of the Committee on Papers and Publications be printed in the journal or elsewhere.

At the regular meetings of the society the order of business shall be as follows: (a) Reading of minutes; (b) Reports of officers, council, and directors; (c) Reports of committees; (d) Reports from local sections in the order of their establishment; (e) Reading of papers and discussions; (f) Miscellaneous business; (g) Announcements; (h) Adjournment.

The regular order of business of the society may be suspended at any session by the consent of three-fourths of the members present.

In the absence of the president one of the vice presidents shall preside, the order of precedence being that of the dates of the charters of the local sections.

New by-laws may be adopted, or the existing ones altered or abolished, at any time by a vote of ten members of the council, provided that a written or printed notice of the proposed change or changes shall have

been sent to each member of the council at least one month before the vote is taken.

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MARCH 7, 1893.

Elwyn Waller presented his resignation as librarian of the society.

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MARCH 11, 1893.

John H. Long, of Chicago, was elected a member of the Committee on Papers and Publications.

Frank T. King, of Brooklyn, N. Y., was elected a member of the Finance Committee *vice* J. H. Stebbins, Jr., declined.

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MARCH 13, 1893.

The following named persons were elected members of the society :

Allen, Dr. E. W., Washington, D. C.  
 Bigelow, W. D., Washington, D. C.  
 Bromwell, William, Washington, D. C.  
 Buchanan, Dr. C. M., Washington, D. C.  
 Byrnes, E. A., Washington, D. C.  
 Cabot, Godfrey L., Boston, Mass.  
 Calkin, W. S., Johnsonburg, Pa.  
 Camp, J. M., Duquesne, Pa.  
 Carmen, J. S., Washington, D. C.  
 Carmody, Professor P., Port of Spain, Trinidad.  
 Carr, Oma, Washington, D. C.  
 Chatard, Dr. Thomas M., Washington, D. C.  
 Cheston, H. C., Washington, D. C.  
 Crampton, Dr. C. A., Washington, D. C.  
 Darton, Nelson H., Washington, D. C.  
 Day, Dr. David T., Washington, D. C.  
 Dewey, F. P., Washington, D. C.  
 Dickerson, Edward N., New York, N. Y.  
 Diller, J. S., Washington, D. C.  
 Earl, Charles, Washington, D. C.  
 Emery, James A., Washington, D. C.  
 Ewell, E. E., Washington, D. C.  
 Fellows, Professor G. S., Washington, D. C.  
 Frerichs, F. W., St. Louis, Mo.  
 Fisher, Samuel T., Washington, D. C.  
 Fuelling, John L., Washington, D. C.  
 Gordon, Professor J. C., Washington, D. C.  
 Griffin, James H., Washington, D. C.  
 Handy, James O., Pittsburg, Pa.  
 Hargrove, J. O., Washington, D. C.  
 Harrington, E. M., Miller, Lake Co., Ind.  
 Hawling, H. H., Washington, D. C.  
 Hayes, Dr. C. W., Washington, D. C.  
 Hillebrand, Dr. W. F., Washington, D. C.  
 Hilton, Samuel L., Washington, D. C.

Hitchcock, Professor Romeyn, Washington, D. C.  
 Hodges, Professor G. C., Utica, N. Y.  
 Holmes, Dr. Jesse H., Washington, D. C.  
 Holton, Frederick A., Washington, D. C.  
 Hunt, Alfred E., Pittsburg, Pa.  
 Johnson, H. M., Washington, D. C.  
 Kelly, Dr. D. J., Washington, D. C.  
 Knorr, Aug. E., Washington, D. C.  
 Krug, W. H., Washington, D. C.  
 Littlewood, Dr. J. B., Washington, D. C.  
 Maxwell, Dr. Walter, Washington, D. C.  
 McDonnell, H. B., College Park, Md.  
 McElroy, K. P., Washington, D. C.  
 Miller, Charles H., Washington, D. C.  
 Mills, James S., Washington, D. C.  
 Packard, Dr. Robert L., Washington, D. C.  
 Pattee, Ernest N., Syracuse, N. Y.  
 Patterson, H. J., College Park, Md.  
 Payne, Henry L., Washington, D. C.  
 Peale, Dr. A. C., Washington, D. C.  
 Read, Professor Albert M., Washington, D. C.  
 Richards, Edgar, Washington, D. C.  
 Rosell, C. A. O., Washington, D. C.  
 Runyan, E. G., Washington, D. C.  
 Sanborn, T. F., Washington, D. C.  
 Sauer, Dr. Ewald, Berlin, Germany.  
 Smith, Edward L., Newport, R. I.  
 Spencer, Dr. G. L., Washington, D. C.  
 Tassin, Wirt, Washington, D. C.  
 Taylor, Dr. Thomas, Washington, D. C.  
 Trescott, T. C., Washington, D. C.  
 Tuttle, Hubert C., Long Island City, N. Y.  
 Von Herff, B., New York, N. Y.  
 Voorhees, Louis A., New Brunswick, N. J.  
 Walton, Dr. J. R., Washington, D. C.  
 Wedderburn, G., Washington, D. C.  
 Wirt, Dr. William Douglas, Washington, D. C.  
 Yeates, W. S., Washington, D. C.

**The following named persons were elected associates:**

Burgess, Herbert L., Providence, R. I.  
 Joy, John A., New York, N. Y.  
 Mallinckrodt, Edward, St. Louis, Mo.

MARCH 30, 1893.

F. E. Dodge, of Brooklyn, N. Y., was elected librarian of the society in place of Elwyn Waller, resigned.

The following was adopted by the council:

"Resolved that the president of the council be and hereby is requested to appoint a committee of three councilors for the purpose of revising and codifying the by-laws of the American Chemical Society."

In accordance with this resolution the president of the council appointed the following named persons as said com-



mittee: Chares E. Munroe, Washington, D. C., Chairman;  
F. W. Clarke, Washington, D. C.; Albert C. Hale, Brooklyn,  
N. Y.

ALBERT C. HALE, Secretary.

### TREASURER'S REPORT FOR 1892.

#### RECEIPTS:

Balance from Treasurer F. T. King.....	\$275.84
Cash received for dues for 1892.....	1,275.97
"    "    "    "    "    1893.....	45.00
"    "    "    arrears of dues.....	25.00
"    "    "    advertisements in Journal.....	258.40
"    "    "    subscriptions to Journal.....	80.75
"    "    "    back numbers of ".....	59.95
"    "    "    initiation fees.....	70.00
"    "    "    balance of Dinner Fund, December 30, 1891...	53.55
"    "    "    "    from New York Meeting Fund, De-	
cember 30, 1891.....	18.75
Cash received for stamped envelopes.....	.34
"    "    "    exchange.....	.11
Total.....	\$2,163.66

#### EXPENDITURES:

Journal.....	\$1,088.95
General expense.....	210.00
Revision of Constitution.....	104.45
Subscription returned (Kenyon).....	6.00
Overpayment on dues returned.....	.10
New York meeting.....	10.00
Hoffman Memorial.....	30.00
Reprints.....	47.65
New York local section.....	85.00
Rochester meeting.....	21.10
Pittsburg ".....	43.00
Balance in Bank of Metropolis, December 31, 1892.....	518.41
Total.....	\$2,163.66

No bills which have been presented and audited up to date remain unpaid.

CHARLES F. MCKENNA, Treasurer.

NEW YORK, December 31, 1892.

FRANK T. KING,	} Auditing Committee.
A. P. HALLOCK,	
DURAND WOODMAN,	

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE ACTION OF AMMONIA GAS UPON MOLYBDENYL CHLORIDE.

BY EDGAR F. SMITH AND VICTOR LENHER.

Received May 26.

IN 1857, Tuttle (*Annalen*, 101, 285) studied the action of ammonia upon molybdenum trioxide and molybdenum chloride ( $\text{MoCl}_3$ ). In the case of the trioxide the temperature at which the reaction was made approached a red heat. The resulting product was in part black in color and possessed metallic luster. Its analysis revealed the presence of nitrogen, hydrogen, and molybdenum. The quantity of the latter constituent equaled 92.9 per cent. Upon conducting the experiment at more elevated temperatures the product was found to contain 77.9 per cent. and seventy-three per cent. of molybdenum, while the hydrogen content did not exceed 0.18 per cent. The results consequently were not constant.

On exposing molybdenum chloride to the action of ammonia gas, at a temperature just sufficient to volatilize the ammonium chloride which arose in the reaction, Tuttle obtained a black, metallic, sintered mass. It was found to contain 82.83 per cent. of molybdenum and was assumed to have the composition expressed by the formula:  $\text{Mo}_3\text{N}_2 + \text{Mo}(\text{NH}_3)_2$ , analogous to a compound of tungsten obtained in a similar manner by Wöhler (*Annalen*, 73, 190).

Several years after the publication of the preceding investigation Uhrlaub presented an inaugural thesis entitled "Die Ver-

bindungen einiger Metalle mit Stickstoff" (Göttingen, 1859), from which we collate the following interesting facts :

In the action of ammonia gas in the cold upon molybdenum chloride much heat was evolved and a black colored product resulted ; its analysis showed the presence of 76.457 per cent. of molybdenum, 23.134 per cent. of nitrogen, and 0.677 per cent. of hydrogen. In subsequent experiments Uhrlaub employed a more intense heat, thus hoping to estimate the slight hydrogen content, but this element continued to show itself in his various products, until on raising the tube in which the reaction took place to an intense red heat he obtained a compound that on careful analysis gave a composition which may be expressed by the formula  $\text{Mo}_3\text{N}_4$ . In other words a molybdenum nitride had been formed by action upon the chloride of the metal with ammonia gas at a high temperature.

When Uhrlaub tried the action of ammonia upon molybdic acid at a gentle heat he obtained " pseudomorphosen," as he designates them, bluish-black in color. Several were prepared ; they varied much in composition. Uhrlaub attributes this variation to the different degrees of heat employed and to the length of time during which the heated molybdenum trioxide was exposed to the action of the gas.

The preceding facts indicate that the action of ammonia gas either upon the trioxide or chloride is not as simple as might be presumed. An amide that might well be expected in either case appears not to have been obtained either by Tuttle or Uhrlaub.<sup>1</sup> We hoped to reach this result by the action of ammonia gas upon molybdenyl chloride in accordance with the equation :



It will be noticed that we apply the term molybdenyl chloride to the compound generally called molybdenum dioxychloride. Our assumption of molybdenyl is based upon the terms sulphuryl, chromyl, etc., applied to compounds possessing a constitution similar to that of the dioxychloride of molybdenum,  $\text{MoO}_2\text{Cl}_2$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{CrO}_2\text{Cl}_2$ .

<sup>1</sup> The primary object of these chemists seems to have been the preparation of molybdenum nitrides.

*Preparation of Molybdenyl Chloride.*—Of the various methods proposed for the formation of this derivative of molybdenum we discovered that the action of dry chlorine on the dioxide of the metal yielded by far the most satisfactory product, both as to purity and quantity. The molybdenyl chloride forms at a very gentle heat quite rapidly and sublimes in feathery crystals. Schulze (*J. prakt. Chem.*, 29 (N. F.) 440) in discussing the action of molybdic acid upon metallic chlorides proposes this procedure for the object we had in view, but we failed to meet with success in our application of the method; the yield was not very abundant.

The crystalline molybdenyl chloride, prepared as just described, was introduced into porcelain boats and these placed in tubes of hard glass, through which we conducted a brisk current of well-dried ammonia gas. The molybdenyl chloride immediately assumed a deep black color, much heat was evolved and copious fumes of ammonium chloride vapor were carried out of the tube. Considerable moisture also collected upon the anterior portion of the combustion tube. At last, heat sufficient to expel any ammonium chloride retained by the compound was applied; but this was not done for a longer period than half an hour. The boat and contents were cooled in ammonia gas. The product of the reaction was placed over sulphuric acid to absorb any retained gas; a portion of it was also washed with water and the aqueous solution examined for chlorine, but this was not found present. In general appearance the product was metallic and black in color. Analyses were made of different preparations. The molybdenum content was determined by oxidizing weighed portions of material with dilute nitric acid, evaporating carefully to dryness, finally applying a gentle heat for a period of fifteen minutes.

The hydrogen was estimated by burning the substance in a current of oxygen, and collecting the water that was produced in a weighed calcium chloride tube.

The nitrogen estimations were three in number; one of them was carried out by the method of Dumas, while the other two were made by the soda-lime process.

The oxygen was obtained by difference.

Our analytical results may be tabulated as follows :

	Substance taken.	MoO <sub>3</sub> found.	Mo, per cent.
1.....	0.1047 gram	0.1156 gram	73.65
2.....	0.1006 "	0.1108 "	73.42
3.....	0.1004 "	0.1110 "	73.70
4.....	0.1028 "	0.1113 "	73.47
5.....	0.1017 "	0.1126 "	73.80

The mean molybdenum percentage of these five determinations is 73.61 per cent.

*Hydrogen determination :*

Substance taken.	Water found.	H, per cent.
0.2088 gram	0.0082 gram	0.43

*Nitrogen determination :*

	Substance taken.	Pt found.	N, per cent.
1.....	0.1510 gram	0.0643 gram	6.05
2.....	0.1529 "	0.0642 "	5.96

The nitrogen found by the Dumas method equaled 6.00 per cent. and the mean of the three nitrogen estimations was also 6.00 per cent.

Two-thirds of this nitrogen content were expelled when our compound was exposed to the action of hydrogen at the highest temperature attainable with a good combustion furnace. Taking the mean of our analyses as a basis for calculation.

	Per cent.
Molybdenum.....	73.60
Nitrogen .....	6.00
Hydrogen .....	0.43
Oxygen (by difference) .....	19.96

We deduce Mo<sub>4</sub>O<sub>8</sub>N<sub>3</sub>H<sub>3</sub> as the most probable empirical formula, which may be variously written to express the enigmatical constitution of this compound. Thus it might be MoO(NH)<sub>3</sub>.MoONH<sub>3</sub>.3MoO<sub>2</sub>, or 4MoO<sub>2</sub>.Mo(NH)<sub>3</sub>, which may be correctly termed tetra-molybdenyl molybdenimide.

Our compound is stable in the air. Hydrochloric acid does not affect it. Nitric acid of sp. gr. 1.42 causes it to burn very energetically. Dilute alkalies attack it very sluggishly. It liberates ammonia when fused with caustic potash; when heated in a current of oxygen it is slowly oxidized. Heated in nitrogen gas the black compound loses water and assumes a reddish color. The analysis of this product indicates that it probably was

molybdenum dioxide mixed with a very small amount of nitride ; at least, traces of nitrogen were found upon examination. Another interesting observation was that when the black product was introduced into an aqueous solution of silver nitrate, crystals of metallic silver gradually appeared over the surface of the molybdenum compound.

We obtained our first product several times, but care must be exercised and the same conditions, noted by us, strictly observed if success in its formation is desired.

An examination of Uhrlaub's analytical results will show that one of his products approaches very closely the compound we have just described. He speaks of it as a black "pseudomorph" with the composition.

	Per cent.
Molybdenum .....	73.55
Nitrogen .....	5.58
Hydrogen .....	0.54
Oxygen .....	20.30

The formula deduced from these figures differs from that presented by us, and what is more, if we understand Uhrlaub correctly, his compounds prepared from ammonia gas and molybdenum trioxide were all "blau-schwarz" in color, and were not acted upon in the cold by nitric acid (see his dissertation pp. 13, 14, 17). However, it is evident that the product we obtained by the action of ammonia gas upon molybdenyl chloride is not the amide we had in view. Thinking that perhaps the heat we applied to drive out the final traces of occluded ammonium chloride may have been sufficient to alter the composition of the product formed at first we allowed the ammonia to act upon the molybdenyl chloride at the ordinary temperature, and when there was no further evolution of ammonium chloride and the boat had become perfectly cold<sup>1</sup>, we introduced carbon dioxide, applying a very gentle heat at the same time, but we failed to achieve our aim. Nitrogen, when substituted for carbon dioxide, gave no better result. We next dissolved molybdenyl chloride in the purest ether we could get and conducted ammonia gas into this solution. We

<sup>1</sup> Portions of the product removed at this stage and shaken with cold water decomposed into a mixture of blue and brown colored masses. The possibility of removing the ammonium chloride in this manner was therefore excluded.

obtained decomposition products. A closer examination of the behavior of the molybdenyl chloride towards ether revealed the fact that the moment the two came in contact a slight hissing sound was perceptible and the ether at once imparted a strong acid reaction to blue litmus. The same was observed when pure chloroform was employed as a solvent.

If molybdenyl chloride be gradually heated in an ammonia atmosphere until the tube of hard glass becomes bright red in color, and the gas action continued for the period of an hour, the resulting product will be an amorphous, metallic, black mass. Subjected to analysis, it gave results as appended :

*Molybdenum Determination :*

Substance taken.	MoO <sub>3</sub> found.	Mo, per cent.
0.1042 gram	0.1061 gram	67.87

*Nitrogen Determination.*—0.1025 gram substance burned with soda-lime gave 7 per cent. nitrogen.

*Hydrogen Determination.*—0.1012 gram substance ignited in a current of oxygen gave 0.0109 gram of water equal to 1.19 per cent. hydrogen.

	Per cent.
Molybdenum .....	67.87
Nitrogen .....	7.00
Hydrogen .....	1.19
Oxygen (by diff.) .....	23.94

The empirical formula deduced from these figures is Mo<sub>4</sub>O<sub>11</sub>N<sub>2</sub>H<sub>10</sub>, which can also be written :

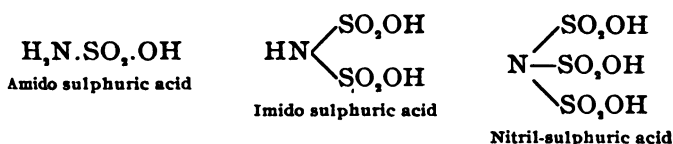


Dilute alkalis have no effect upon this compound ; but it liberates ammonia when fused with caustic potash. It is converted into molybdenum trioxide very energetically, with evolution of sparks, when brought in contact with cold nitric acid.

Other products were obtained by us. Their analyses lead us to the conclusion that with us, as with Uhrlaub, the composition of the derivative depended wholly upon the length of time during which the gas acted upon the molybdenyl chloride, and upon the degree of heat employed in the experiment. It seems highly improbable to us that the amide, MoO<sub>3</sub>(NH<sub>3</sub>)<sub>2</sub>, molybdenyl amide, can be prepared after the fashion pursued by us,

for it is quite certain that the heat of the reaction evolved in the first contact of the ammonia with the molybdenyl chloride exercises a very potent influence upon the composition of the product.

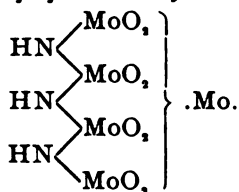
When we recall the action of ammonia gas upon sulphur trioxide and sulphuryl hydroxychloride resulting in the formation of compounds of the following constitutions:



the question that obtrudes itself is, are not these products and their methods of formation types of the processes and results that have occurred not only in our studies described in this paper, but also in the studies of Tuttle and of Uhrlaub?<sup>1</sup> Are not their products, as well as our own, only residues of amido, imido, and nitrilo-molybdic acids? Above we have written for our first product the constitutional formulas,



but after considering the sulphur types we would express our empirical formula  $\text{Mo}_4\text{O}_{12}\text{N}_4\text{H}_4$  differently as follows:



We have here several broken down molybdenyl amide nuclei in conjunction, not chemically combined, with metallic molybdenum. Reviewing the behavior of the product which we thus graphically represent, we may be allowed to emphasize the fact that when it was brought in contact with an aqueous argentic nitrate solution metallic silver was precipitated, and this we know from an observation of Smith (*Ztschr. anorg. Chem.*, 1, 360) is a property of metallic molybdenum. Further, it will be

<sup>1</sup> At least in so far as the action of ammonia gas upon molybdenum trioxide was concerned.



recalled that when our product was heated in an atmosphere of nitrogen it left a reddish colored compound that, upon analysis, approximated the requirements of molybdenum dioxide, and that traces of nitrogen were also detected in it. All these experimental facts find expression in our graphic representation above.

The second product obtained by us was even more active when introduced into a silver nitrate solution, throwing out metal quite rapidly, proving in our opinion the presence in it of even a greater quantity of metallic molybdenum than is contained in the first body. Similar reduced molybdenyl amide nuclei, mixed with metallic molybdenum, could also be constructed for our second compound and be in harmony with the observed deportment of this body if it were necessary.

UNIVERSITY OF PENNSYLVANIA,  
MAY 16, 1893.

### ACTION OF AMMONIA GAS UPON WOLFRAMYL CHLORIDE.

BY EDGAR F. SMITH AND OWEN L. SHINN.

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THE results obtained by Smith and Lenher in their investigation of the action of ammonia gas upon molybdenyl chloride suggested the idea of making similar research with tungsten, chiefly for the sake of comparison. It will be recalled that Wöhler (*Annalen*, 73, 190) carried out a careful investigation on the behavior of ammonia toward both tungsten trioxide and tungsten chloride. He succeeded in preparing by the first process the compound  $3\text{WN}_3 + \text{W}_2\text{N}_4\text{H}_4 + 2\text{WO}_3$ , and by the second, the compounds  $2\text{WN}_3 + \text{WN}_4\text{H}_4$  and  $\text{W}_2\text{N}_4 + \text{WN}_4\text{H}_4$ . These experiments did not yield either a simple nitride, or an amide. They were, however, the patterns for the later investigations of Tuttle and those of Uhrlaub, although their final results were in reality not what they had hoped to get. The attempts of Smith and Lenher were not any more fruitful, when we remember that they sought to prepare molybdenyl amide,  $\text{MoO}_3(\text{NH}_3)_2$ . While a like result was naturally to be expected

in the action of ammonia upon wolframyl chloride,  $\text{WO}_2\text{Cl}_2$ , it seemed to us to be worth the while to develop as much light upon the reaction as possible. Hence it was followed with the results that will appear later.

*Preparation of Wolframyl Chloride,  $\text{WO}_2\text{Cl}_2$ .*—We experienced no difficulty in getting this derivative by the direct action of dry chlorine upon the dioxide of the metal. It is true that slight amounts of tungsten oxytetrachloride were formed simultaneously, but these were quite easily and quickly eliminated by exposing the  $\text{WO}_2\text{Cl}_2$  to a very gentle heat in an atmosphere of carbon dioxide. The resublimed product was employed by us in the experiments which were made.

*Wolframyl Chloride and Ammonia.*—The wolframyl chloride was placed in porcelain boats and these introduced into a hard glass tube through which a brisk current of dry ammonia gas was conducted. It will be recalled that the moment the gas came in contact, at the ordinary temperature, with the molybdenyl chloride, the latter at once assumed a deep black color, clouds of ammonium chloride, water, and much heat were evolved. With wolframyl chloride and ammonia there was no visible sign of action. The chloride remained unaltered even after the gas had passed over it for an hour. We thus observe here a marked difference in the conduct of these two similarly constituted chlorides,  $\text{MoO}_2\text{Cl}_2$ , and  $\text{WO}_2\text{Cl}_2$ , towards ammonia, the first being exceedingly reactive, while the second was absolutely inert, at least at the ordinary temperature. Upon applying heat to wolframyl chloride while exposed to the ammonia vapor, a slow change began. Fumes of ammonium chloride were evolved, and in time the entire mass became black in color. It was not until an intense heat was applied that the product became uniform in appearance. When ammonium chloride ceased to be formed the boat and contents were allowed to cool in ammonia. The metallic mass was allowed to stand over sulphuric acid during the night in order that any adhering ammonia might be absorbed. Portions of it were also examined for chlorine, but this was not found.

*Tungsten Determination.*—The material was evaporated several times to dryness in a porcelain crucible with moderately

concentrated nitric acid. The residue was then heated for a period of fifteen minutes with the direct flame. The tungstic acid was bright yellow in color and free from lower oxides.

	WO <sub>3</sub>	W. per cent.
(a) 0.1025 gram substance gave 0.1106 gram		= 85.75
(b) 0.1028 " " " 0.1108 "		= 85.49

*Nitrogen Determination.*—The estimations were made by igniting the substance with soda lime.

	N.	N. per cent.
(a) 0.1054 gram substance gave 0.00744 gram		= 7.06
(b) 0.1009 " " " 0.00665 "		= 6.60

*Hydrogen Determination.*—0.1609 gram substance gave 0.0028 gram water, equal to 0.193 per cent.

The preceding percentages led to the empirical formula,  $W_3N_2O_4H_2$ , which could also be graphically written so as to indicate the presence of broken down wolframyl amide nuclei, just as was done by Smith and Lenher in their discussion of the constitution of the products obtained from molybdenyl chloride and ammonia.

Our tungsten derivative is jet black in color, and it is insoluble in water. Hydrochloric acid is without action upon it. Concentrated nitric acid oxidizes it very rapidly with the evolution of sparks. Dilute alkalis do not alter it, but fusion with caustic potash liberates ammonia gas. When introduced into an aqueous solution of silver nitrate it causes the separation of crystals of metallic silver. This behavior we assume to be indicative of the presence of metallic tungsten in the compound, for it has already been observed that metallic tungsten, like metallic molybdenum,<sup>1</sup> precipitates silver quantitatively from its salt solutions. Hoping that we might perhaps obtain direct evidence of the presence of the group  $WO_3$  (which we believe to be present) if we dissolved our product in sulphuric acid and then titrated with potassium permanganate, we made this attempt. We heated the black material with sulphuric acid (sp. gr. 1.8) in sealed tubes for several days at temperatures ranging from 180°–250°, but it was unaltered. We must therefore be satisfied to represent our reaction product as we have already represented it, and abstain from any graphic formulation as was

<sup>1</sup> *Ztschr. anorg. Chem.*, 1, 360.

done with the molybdenum derivative, although by analogy we might deduce a similar structure. We tried the action of ammonia upon wolframyl chloride suspended in ether (it is not soluble in this menstruum), and also in chloroform, but obtained green colored decomposition products.

Our experiments demonstrate: (1) that wolframyl chloride behaves very differently from molybdenyl chloride at the ordinary temperature when exposed in an atmosphere of ammonia; (2) that the reaction product is not a true amide, but in all probability a union of disintegrated amide molecules; and (3) that metallic tungsten is present in the product.

UNIVERSITY OF PENNSYLVANIA,  
May 23, 1893.

### DETERMINATION OF ORGANIC MATTER BY MOIST OXIDATION.

BY H. HEIDENHAIN.

ANY chemist who has carried out combustions by the ordinary dry process knows how much time is required, and what care must be observed, to obtain results of practical value. In technical work, where time is limited, the combustion process is resorted to only when nothing else will give the desired result.

Many attempts have been made to shorten and simplify the general process of organic elementary analysis, but for carbon and hydrogen we have, as yet, no process which accomplishes what the Kjeldahl method does for nitrogen.

I have tried to solve this problem by employing a wet method in place of the ordinary dry one. The advantages of a wet process are evident. First, the trouble of preparing the copper oxide, or substitute, would be saved. Besides this, it would not be necessary to have the substance in the dry condition, and finally, much simpler apparatus could be used. Instead of the combustion tube and the combustion furnace, a simple burner and a flask may be used.

I am sorry to say that, at the present time, the methods of combustion by the wet process have not been improved so much that all substances can be determined. What has been

accomplished in solving the problem, I will explain in the following :

There are two substances which are used as oxidizing materials for combustion by the wet process—permanganate of potash and chromic acid—the latter as free chromic acid and in the form of bichromate of potash. Both oxidize in presence of sulphuric acid. The permanganate is used only for a few special purposes, namely for the oxidation of oxalic acid, the well-known quantitative method for determination of glycerine according to Planchon, whereby the oxidation is not a complete one, and finally, for determination of the organic matter in water, a method which does not give absolute, but only relative results. More generally chromic acid is employed.

The oldest directions in regard to employment of a chromic acid and sulphuric acid mixture for the determination of carbon seem to be those of the Rogers Brothers, published in 1847. The authors mentioned worked with a highly concentrated sulphuric acid, namely five parts of acid and one part of water, and used bichromate of potash. They employed the method only for determination of carbon in graphite, which can be oxidized only with great difficulty by the dry process. The carbonic acid developed was absorbed by an absorption apparatus and was weighed.

Ullgren improved this method by using free chromic acid instead of bichromate, in order to prevent the formation of sulphate of chromium and potassium, which covered the particles of carbon so that the mixture could not act upon them. Ullgren employed this method also for the determination of carbon in iron and steel. He worked with a mixture less strong than that used by Rogers. His method is found in all manuals of quantitative analysis, and is preferred in general to the dry combustion process.

It was only one step further to employ these methods in the determination of the carbon in carbon compounds. Bossingault first did this. Unfortunately, I have not been able to find any of the particulars of his method.

Messinger used no new principle in this method as applied by him. He worked usually with 0.15–0.35 gram sub-

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stance, five to six grams chromic acid or bichromate, and thirty-three cc. sulphuric acid. He heated only slightly. He says that he got good results with almost all substances; only with very volatile substances he did not succeed. He varied his method according to circumstances, and prescribed special methods for substances containing sulphur, phosphorus, arsenic, antimony, chlorine, bromine, and iodine. In all cases he weighed the carbonic acid.

Legler used the chromic acid mixture only for a special purpose, namely for determination of glycerine. He took 0.75-1 gram of the substance, and heated for each one-fourth gram one hour. In contradistinction to the methods mentioned above, Legler operated in the so-called "two-flask" apparatus, whereby the carbonic acid was calculated from the loss of weight. This seems, at first, to be of no importance, but is really of great importance.

All methods described suffer from a fundamental error. The merit of detecting this error belongs to Cross and Bevan, who worked in company. They tried to oxidize cellulose by the chromic acid mixture, and did that first in the "two flask" apparatus according to Legler, and then for control, according to Ullgren. The results of these two methods did not agree. They assumed that in the process of oxidation, not only carbon dioxide, but also the monoxide, was formed. They tested, therefore, the gas developed by both methods, and found carbon monoxide in both cases. Of course, the error must be larger in those methods in which the carbonic acid is weighed in an absorption apparatus, than in those in which it is shown by the loss of weight. In the latter, only the second atom of oxygen, which ought to oxidize the monoxide to dioxide, escapes observation, while in the first the whole of the carbon monoxide escapes. The error must be in the proportion of 16:44. Cross and Bevan prevented this error in theory perfectly by measuring the gases, as carbon monoxide and carbon dioxide contain the same amount of carbon in the same volume. In practice there were some difficulties. A concentrated mixture of chromic and sulphuric acid develops oxygen when heated, and that had to be prevented. Therefore they determined

the proportion of the ingredients in which the evolution of oxygen below  $100^{\circ}\text{C}$ . did not take place. At the end of the operation the liquid has to be heated to accomplish oxidation and to remove carbon dioxide from the solution. A little will remain, nevertheless, because the solution will not boil at  $100^{\circ}\text{C}$ ., as it contains sulphuric acid and salts. For this reason a correction for the absorbed carbon dioxide is necessary.

The method is, briefly, as follows :

Take enough of the substance to develop 90–100 cc. gas. The substance is dissolved in nine cc. sulphuric acid, and chromic acid is added in excess of thirty per cent. First, the temperature is kept between  $60^{\circ}$ – $70^{\circ}$ , then raised to  $100^{\circ}$ . Cross and Bevan published very good results. Only fatty acids and bases containing nitrogen could not be oxidized completely.

Cross and Bevan's discovery of the carbon monoxide in the products of oxidation called the attention of Professor Fresenius to the same point. Fresenius engaged Widmer to criticise Ullgren's method. Widmer found that also in the oxidation of graphite carbon monoxide is formed. He proved that by passing the gases leaving the absorption apparatus over heated copper oxide, carbon dioxide was produced. He determined the quantity, and found the surprising result that the error amounted to 6.58 per cent. to 4.72 per cent. in a graphite containing about ninety per cent. of carbon. In order to get correct results, it is necessary to oxidize the carbon monoxide in the current of gas before it reaches the absorption apparatus, by passing the same through a small combustion tube.

Hehner, who, like Legler, employed the chromic and sulphuric acid mixture for determination of glycerine, introduced a new principle in these methods. He did not weigh or measure the products of oxidation, but determined the amount of oxygen used for oxidation. Hehner took 0.4 gram substance, dissolved in twenty-five cc., added 40–50 cc. of a concentrated solution of bichromate and fifteen cc. sulphuric acid. This mixture was heated two hours in a water-bath. Then it was diluted, and the chromic acid, which remained intact, determined. He convinced himself that glycerine, in this way, was completely oxidized, and found at the same time that the soluble fatty acids remained intact.

Kjeldahl has recently published a method of combustion by chromic acid, but I am not acquainted with the details as worked out by him.

I wish now to explain the method as employed by myself. In some respects it resembles the Hehner method, and was first carried out in detail in the laboratory of Dr. Endemann, in New York, some three years ago, although work had been done on it several years earlier.

I employ in this process: (1) A  $\frac{N}{8}$  solution of potassium bichromate; (2) chemically pure sulphuric acid; (3) the usual volumetric apparatus for titration; (4) solutions of potassium ferricyanide and ferrous sulphate or ammonium ferrous sulphate; (5) the apparatus shown in the cut, the characteristic feature of which is the condenser. This is inserted in the neck of the boiling flask, so that the condensed vapors come



in contact with glass only; (6) the solution of the substance to be examined, which should not be stronger than  $\frac{N}{8}$ .

The method is carried out as follows: Twenty-five cc. of the solution of the substance is mixed with thirty cc. of the  $\frac{N}{8}$  solution of potassium bichromate, and then thirty-three cc. concentrated sulphuric acid are added. The whole mixture is heated on a wire gauze until it begins to boil. Then the flame is regulated so that the liquid boils up from time to time. During the heating the return condenser is kept in action. Most of the vapors are condensed; small losses of the volume are of no importance. After boiling is continued for ten minutes the flask is removed from the flame, and the excess of chromic acid is determined in the usual manner. I must mention here that it is not necessary to cool or to dilute the solution before titration.

The above-mentioned proportions of the solution of the sub-



stance of chromic acid solution and sulphuric acid are not accidental, but are the result of a number of experiments in regard to which I want to say a few words, as they are of importance.

It is desirable to use as much sulphuric acid as possible in order to act energetically upon the organic substances, and to get high temperatures. On the other hand, a decomposition of chromic acid by the sulphuric acid alone must be prevented. To find the proper proportion I heated mixtures of  $\frac{N}{8}$  potassium bichromate and sulphuric acid alone for thirteen minutes. I started with very large quantities of sulphuric acid and reduced the same gradually, until the point was found where the decomposition was so small that it could be neglected.

For instance, I took in a first experiment 23 cc.  $\frac{N}{8}$   $K_2Cr_2O_7$  + 30 cc.  $H_2SO_4$ . The decomposition corresponded to 2.65 cc.  $\frac{N}{8}$   $K_2Cr_2O_7$ . Then I took 23 cc.  $\frac{N}{8}$  solution + 20 cc.  $H_2SO_4$ . The decomposition amounted to 0.25 cc.  $\frac{N}{8}$ . Finally, I took 23 cc.  $\frac{N}{8}$  + 15 cc.  $H_2SO_4$ . The decomposition was 0.05 cc.  $\frac{N}{8}$   $K_2Cr_2O_7$ .

Purposely, I stopped here, and did not reduce the sulphuric acid any more, as, firstly, an error of one-half tenth of one cc. is very small and it may be neglected with safety; secondly, as the error must be still smaller in practical determinations, because the main quantity will be reduced inside of the first minute. Therefore, the decomposition of chromic acid by action of the sulphuric acid alone can take place only in the excess of added chromic acid. This excess is about five cc. or one-fifth of the quantity used in the blank experiment. Therefore, the decomposition cannot be larger than one-fifth of five-hundredths on one cc. or one-hundredth of one cc.

Further, these five cc. are present in a volume of  $25 + 30 + 33 = 88$  cc. in a practical determination, while the twenty-five cc. in the blank experiment was present in  $25 + 15$  cc. = 40 cc. The dilution in the first case is eleven times larger than in the latter one. I will not say that the error is only one-eleventh of 0.01 cc., but I am sure it is not larger than 0.01 cc. An error of 0.01 cc. may be neglected without scruple.

Speaking of the practical use of the method, I do not claim that it is suitable for general use. On the contrary I would

wish to have it considered only as an empirical one. Quantitative oxidation is possible only with a small number of substances, but almost quantitative results are obtained with very many substances. The method has, in my own opinion, about the same value as Allihn's method for determination of sugar with Fehling's solution. In a very similar manner it will be necessary to make tables in which the results empirically found are registered. I have commenced already to do this. I found that the oxidation is the more complete the larger the excess of chromic acid has been. In general, the figures run so close that it was sufficient to determine two points of the table, namely for 100 per cent. and for 40 per cent. All other points may be obtained near enough by interpolation.

For the advantages of my method in comparison with other ones, I may mention that it is a quick one, and requires only very small quantities of substance. In parallel determinations I obtain very close results, which is due to the fact that all the conditions of the experiment can be easily followed. In conclusion, I will give a short table of results by way of illustration.

Name of substance.	Oxidized by a concentration equivalent to	
	$\frac{N}{8}$	$\frac{2N}{17}$
Oxalic acid .....	100.00 per cent.	100.00 per cent.
Tartaric acid .....	(1) 99.48	99.75
" " .....	(2) 99.56	....
Dextrose .....	98.45	99.90
Corn starch, commercial:		
With 11.66 per cent. moisture..	84.8	....
" 10.34 " " " ..	85.6	....
" 12.09 " " " ..	84.4	....
" 12.15 " " " ..	85.2	....
Average, 11.56 " " " ..	85.0	....
Purest glycerine from Schering....	(1) 97.50	....
" " " " ....	(2) 97.73	....
" " " " ....	(3) 97.65	....
Acetic acid .....	0	0
Alcohol <sup>1</sup> .....	33.6	....
Alpha-naphthol .....	75.0	....
Beta-naphthol .....	83.0	....
Benzoic acid .....	Very little more than 90 per cent.	
Salicylic acid .....	" " " " " " " "	" " " " " " " "
Morphine .....	61 per cent.	

CHICAGO, JANUARY, 1893.

<sup>1</sup> This experiment was made with a measured quantity, therefore not absolutely correct. I assume that alcohol will be oxidized exactly to acetic acid, and the result will be just 33½ per cent.

# SOME PRODUCTS OF CASSAVA.<sup>1</sup>

BY E. E. EWELL AND H. W. WILEY.

SOME four years ago one of us<sup>2</sup> described a plant which has been grown in Florida for many years under the name of sweet cassava, the botanical name of which is *Jatropha manihot* or *Aipi*. From the analyses made at the time it was found that the plant was valuable for feeding purposes, being very rich in carbohydrates, although rather poor in albuminoids. Lately the subject has been studied to a much greater extent, with the object of preparing as large a number of products as possible from the plant, with the determination of their chemical properties and food values.

A large quantity of the root was obtained from Florida, the bark separated from the root, and each subjected to analysis with the following results :

	Peeled root.		Fiber after removal of starch.		Bark of root.	
	Fresh.	Dry.	Fresh.	Dry.	Fresh.	Dry.
Moisture .....	61.30	....	....	....	61.30	....
Ether extract.....	0.17	0.44	0.30	0.66	0.66	1.70
Albuminoids, (nitrogen × 6.35).....	0.64	1.66	1.02	2.29	2.29	5.91
Starch (diastase extract inverted with HCl)...	30.98	80.06	64.64	....	....	....
Fiber.....	0.88	2.26	10.68	3.83	3.83	9.89
Ash .....	0.51	1.31	1.42	2.02	2.02	5.23
Undetermined .....	5.52	14.27	21.94	29.90	29.90	77.27
	100.00	100.00	100.00	100.00	100.00	100.00

With the starch in the analysis given above is reckoned also the soluble carbohydrates, consisting almost exclusively of cane sugar, and of which in an analysis of another portion of the dry substance as high as seventeen per cent. was found. The undetermined portion consists of the digestible fiber and carbohydrates of the pentose series. The pentosans in the fiber were determined by the furfural process as modified by Krug, and the amount in the air-dried material was found to be 3.92 per cent., and in the material after the removal of the starch 5.33 per cent.

<sup>1</sup> Read before the Washington Chemical Society, February 9, 1893.

<sup>2</sup> Wiley, *Agric. Science*, Vol. 2, No. 10, p. 256 et seq.

The fresh root was found to contain 38.7 per cent. of dry matter, being considerably more than was found in the fresh sample of the previous analysis. Of this 38.7 per cent., 30.98 consisted of starch and soluble carbohydrates.

Experiments were made to determine the yield of air-dry starch which could be obtained from the roots by laboratory work. Two sets of experiments were made. In the first set the roots were pulped on a Pellet rasp used for preparing beet pulp for instantaneous diffusion. Twelve kilos of the unpeeled root were rasped in this way and the starch separated by washing through a sieve of bolting-cloth. The washings and settlings were collected and dried in the ordinary method of starch manufacture. The yield of pure starch was 3105 grams, equivalent to 25.9 per cent. of the total weight of the root. The starch was almost absolutely pure, containing only a trace of nitrogenous matter. In the second experiment ten kilos of the root were ground in a pulping machine used for preparing green fodder for analysis. The pulp was much less fine than that produced by the Pellet rasp. Treated in the same way, the yield of air-dry starch was 2360 grams or 23.6 per cent. One of the striking points in connection with the work is that the residue from the starch, which consisted largely of fiber, as will be seen by reference to the above analysis, contained still a large percentage of starch, showing that by the process employed, the whole of the starch was not secured from the pulp.

The cassava which grows in tropical regions contains a notable percentage of hydrocyanic acid, so great in fact that it can not be used directly as a food. The so-called poisonous cassava is boiled to expel the hydrocyanic acid before being used for feeding purposes. A careful determination was made of the hydrocyanic acid in the fresh root, and the amount was found to be 0.015 per cent. While this shows a considerable quantity of hydrocyanic acid, it is hardly in proportions sufficiently large to be alarming. Nevertheless, any possible danger could be avoided before using the material as a food by subjecting it to a sufficient heat to expel the hydrocyanic acid. The hydrocyanic acid seems to be distributed throughout the pulp, and particularly in the juices, which can be expressed from the

pulp. No injurious effect from the hydrocyanic acid has ever been observed in the case of animals fed on cassava in Florida. The bark of the root was also subjected to analysis, as will be seen by reference to the table. It contained no starch, the undetermined matter being chiefly digestible fiber and pentosans.

The mineral matters extracted from the soil are distributed as indicated in the table. The amount of ash in the root itself is quite low, showing that the cassava plant does not require a soil very rich in mineral constituents. The amount of mineral matter taken from the soil by 100 kilos of the fresh root is approximately only half a kilo. The albuminous matters are also present in small quantities, being only slightly larger in weight than the ash itself. The plant, therefore, is one which seems particularly suited to feed almost exclusively from the air and water, and hence is one which could be recommended on the sandy soils of Florida as a crop which would require the minimum of fertilization.

#### COMPOSITION OF THE ASH.

The ash of the peeled root and the bark of the root was subjected to analysis with the following results :

##### ANALYSES OF THE ASH OF CASSAVA ROOT.

Constituents.	Peeled root.			Bark of root.		
	A.	B.	Mean.	A.	B.	Mean.
Carbon .....	0.30	0.31	0.31	0.79	0.77	0.78
Silica (soluble in solution of $\text{Na}_2\text{CO}_3$ ) .....	0.97	0.91	0.94	10.53	11.36	10.94
Silica (insoluble in solution of $\text{Na}_2\text{CO}_3$ ) .....	7.15	7.15	7.15	52.99	52.16	52.58
Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) ...	0.66	0.66	0.66	2.46	2.44	2.45
Calcium oxide ( $\text{CaO}$ ) ..	10.63	10.64	10.64	6.58	6.65	6.62
Magnesium oxide ( $\text{MgO}$ )	7.36	7.35	7.36	3.31	3.33	3.32
Sodium oxide ( $\text{Na}_2\text{O}$ ) ..	1.12	1.28	1.20	0.84	1.05	0.95
Potassium oxide ( $\text{K}_2\text{O}$ )	41.72	41.54	41.63	14.73	14.68	14.70
Phosphoric acid ( $\text{P}_2\text{O}_5$ )	15.58	15.59	15.58	2.44	2.46	2.45
Sulphuric acid ( $\text{SO}_3$ )...	3.67	3.80	3.73	1.71	1.71	1.71
Carbonic acid ( $\text{CO}_2$ )....	9.15	9.12	9.14	2.53	2.50	2.51
Chlorine ( $\text{Cl}$ ).....	2.76	2.75	2.75	1.41	1.42	1.41
Total .....	101.07	101.10	101.08	100.32	100.53	100.42
Oxygen equivalent to chlorine .....	0.62	0.62	0.62	0.31	0.31	0.31
Difference .....	100.45	100.48	100.46	100.01	100.22	100.11

From the above numbers it is seen that the ash of the peeled root is especially rich in potash, almost one-half of the total weight being composed of this substance. The potash is combined chiefly with carbonic and phosphoric acids. In the ash of the bark, as might be expected, silica is the predominating element, more than half the total weight consisting of this substance.

Assuming a yield of five tons of roots per acre, the weights of the important fertilizing materials removed by such a crop can be readily calculated from the data given.

Since the bark forms approximately 2.2 per cent. of the entire root, the total crop would be made up of the following amounts of bark and peeled root, which would contain the amounts of mineral given below :

Peeled root	9780 lbs.,	containing	49.88 lbs. ash.
Bark of root	220 "	"	4.44 " "
	10,000 "	"	54.32 " "

The more important mineral matters contained therein are :

	Ash from peeled root. 49.88 lbs.	Ash from bark. 4.44 lbs.	Total ash from 5 tons. 54.32 lbs.
Lime (CaO) .....	5.31 lbs.	0.29 lb.	5.60 lbs.
Magnesia (MgO) .....	3.67 "	0.15 "	3.82 "
Potash (K <sub>2</sub> O) .....	20.77 "	0.65 "	21.42 "
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> ) ...	7.77 "	0.11 "	7.88 "
			38.72 "

The less valuable mineral plant foods—that is, those which are of so little note as to require no conservation or addition—amount to 17.60 lbs. per acre.

Quite a number of preparations was made from the starch of the root, and among them may be mentioned : First, tapioca. The first portions of starch washed out, especially, produce an excellent article of tapioca when moistened and dried in the proper way. Second, glucose. Both the fresh root and the extracted root yield full theoretical amounts of glucose, and samples of this article were made by the conversion of the starch both by sulphuric acid and diastase. The samples of glucose made from the starch were exceptionally good, especially when diastase was used, the glucose in this case containing large quantities of

maltose. Commercially it would be more probable to make the glucose directly from the fresh root, in which case the considerable percentage of cane sugar contained by it would be saved, whereas if glucose is made from the starch the cane sugar is previously washed out. On account of the presence of the bark, however, the glucose made from the whole root is not so fine in quality as that made from the pure starch. Third, alcohol. The glucose on fermentation affords the usual quantity of alcohol. Fourth, cane sugar. A beautiful preparation of cane sugar was made from the water used in washing out the starch. The amount of cane sugar, however, is not large enough to warrant its extraction on a commercial scale from the waters used for washing. It is, however, present in sufficient quantity to indicate that in making glucose it is better to use the whole root as indicated above.

The general result of the analytical work is such as to establish the fact that the cassava is a plant of high economic value and worthy the attention of those interested in the carbohydrate products of the country.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE; SENT BY H. W. WILEY.—No. 3.]

### AIR DRYING OVEN.

BY DR. G. L. SPENCER.<sup>1</sup>

Received May 3, 1893.

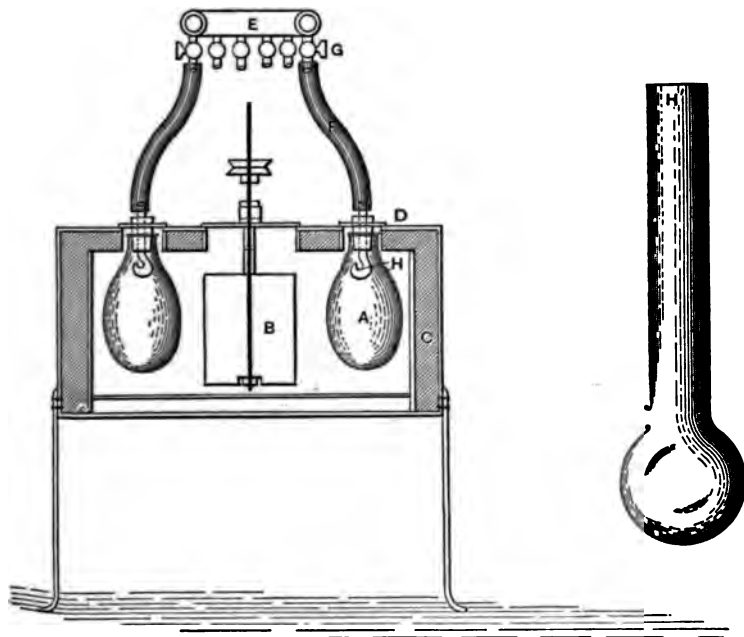
THIS oven is made of Russia iron, with double walls, and is cylindrical in shape. The walls are about one inch apart, and the space between them is filled with some non-conducting material; plaster of Paris is very convenient for this purpose. The bottom of the oven is also double, the outer bottom being made of Russia iron and the inner bottom—placed at a distance of one-half an inch from the outer one—is made of copper. The space between the two is filled with air. The object of having the inner bottom of copper is to allow a speedier and more even distribution of the heat, which is imparted from a lamp placed below the outer bottom. The top of the oven is also made double, with perforations sufficiently large to admit

<sup>1</sup> Presented to the Washington Chemical Society. April 13, 1893.

the drying flasks. The space between the tops is also filled with some non-conducting material like plaster of Paris.

After the flasks are placed in position the open space is closed by a cover, in the center of which is a hole through which the neck of the flask passes. The oven is heated with a cylindrical, flat, copper lamp, which is regulated by an ordinary mercury regulator. The air within the oven is kept in motion by a fan, B, driven very conveniently by a small toy engine connected with the exhaust or compressed air service.

The drying flask, A, is made with a rounded bottom, and its

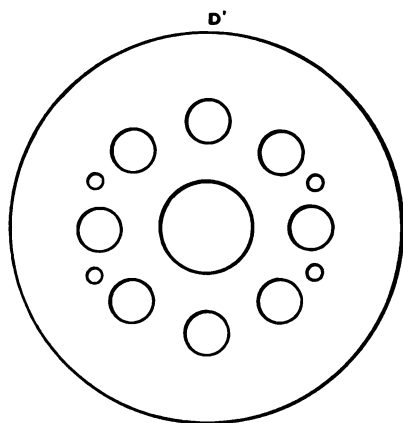


content ranges from 150 to 200 cc. It is closed with a rubber stopper carrying a water trap bulb, H H', arranged in such a way that the vapor of water which condenses within the exhaust tube, instead of falling back into the flask, remains trapped in the water bulb. All the flasks in the oven are connected by means of a common connection, E, with a vacuum pump capable of producing a vacuum of from twenty-six to twenty-seven



inches. The temperature at which the drying is to be made can be fixed at any desired point, from low temperatures up to as high as can be safely used without charring the material to be desiccated. For ordinary work the lamp is set for a temperature of  $100^{\circ}$ .

From six to eight of these drying flasks are connected *en batterie* with the pump. Each one can be connected or disconnected with the pump by its stop-cock G. If a current of hydrogen is to be introduced into the drying flask it is easily



accomplished by passing a very small glass tube through the cork, joined to another tube by a rubber connection immediately below the cork. The inner tube should pass nearly to the bottom of the flask and be weighed with it. The hydrogen is sucked into the flask, passing through a wash-bottle containing caustic soda and then sulphuric acid and over solid potash. The speed of the current, which

need not be very great, is controlled by a stop- or pinch-cock. Any of the sample which may touch the inner tube during the intumescence caused by desiccation remains thereon and is weighed at the end with the tube which is detached and left in the drying bulb.

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### THE RIVER NILE.

BY H. DROOP RICHMOND, LATE SECOND CHEMIST TO THE EGYPTIAN GOVERNMENT.

*Continued from p. 42.*

IN order to more readily compare the different analyses, I adopted a modification of Wigner's scale (*Analyst*, IV, c. f. Muter, *Analyst*, 8, 93). I do not agree with Wigner that a scale can be constructed for all waters, but I am of opinion that in a case like this, when a number of waters of the same origin have to be compared, that it is of use, though not of rigid exactitude. I

wish to state distinctly that my scale is for the water of the Nile *only* after double filtration through paper (and in a few other occasional cases).

In drawing up my scale and limits I took into account the origin of the impurities in the Nile, its rapid self-purification, the absence of nitrates, and other small points; the task of giving all the reasons in detail would be too difficult and lengthy to permit their publication in a paper of this kind, and I give the scale adopted without further comment.

Each 0.005 part of free ammonia .....	= 1
“ 0.001 “ albuminoid ammonia .....	= 1
“ 0.005 “ oxygen absorbed in fifteen minutes..	= 1
“ 0.01 “ “ “ “ four hours .....	= 1
“ 0.2 “ nitric acid .....	= 1

For Letheby's and Pollard's analyses

Each 0.005 part of oxygen absorbed..... = 1

The limits I propose, are:

Good water up to about 50.

Moderate water from about 50 to about 100.

Bad water over about 100.

This value I term “coefficient of purity.”

In the case of waters from Wady Halfa, Assouan, and Keneh, the time of transit was longer than is desirable, and I have corrected their coefficient of purity by adding 100 per cent. to the Wady Halfa analyses, sixty per cent. to the Assouan analyses, and forty per cent. to the Keneh analyses. The figures are based on my experiments on the self-purification of the water, and give rough approximations. I have thought it more useful to employ these approximations than to reject the analyses altogether, but they can only be regarded as giving general indications.

I have had to reject the Minieh results for reasons stated below. In order to compare the results in Table V their averages are given in Table VI; the Bahr Yousef results in Table VIII are also averaged.

The methods of the Society of Public Analysts were adopted with the following modifications:

- (1) The total solids were dried at 150° C.
- (2) The nitric acid was determined by the copper-zinc couple

(Williams, *J. Chem. Soc.*, 1881, 100), nine-tenths of the free ammonia being subtracted, and the remaining ammonia multiplied by 3.2 to give the quantity of nitric acid; these constants were experimentally determined for the Nile water.

(3) The suspended matter was determined by evaporating a known quantity of unfiltered water, drying at  $150^{\circ}$ , and subtracting the total solids of the filtered water.

An inspection of the tables and diagrams leads to the following conclusions :

(a) The total solid sand chlorine increase regularly during the flow of the river.

(b) The coefficient of purity decreases regularly, showing a continual purification.

(c) The nitric acid is very small.

(d) The Nile in its passage through Cairo undergoes slight, but distinct pollution.

(e) The Nile water on standing purifies itself (this has been otherwise confirmed).

Conclusion (a) is especially brought out by the results on the Bahr Yousef and the Lower Nile, where the current is less rapid than on the Upper Nile.

(f) Filtration purifies the water of the Nile. This will be more fully discussed under part III.

The results at Rosetta have been rejected on account of the small number of analyses, and those of Minieh because there is evidence of the samples not having been taken in accordance with directions; the Nile at Minieh is very wide (one and a half miles) and near the town the water is very shallow and has practically no current, and it is more than probable that the samples were taken at a short distance from the bank instead of in mid-stream. The occurrence of nitric acid at some parts and its disappearance at others caused at first some surprise, but this is probably due to the fact that the bed of the Upper Nile contains iron in the forms of ferrous and ferric silicates and magnetic oxide in considerable quantities, pointed out by Johnson Pasha and myself in a communication to the Geological Society. The absence of nitric acid at Port Said is due to the fact that the water is conveyed many miles in iron pipes; a similar disappearance of nitrates

from a like cause is recorded by Harvey (*Analyst*, 14, 34); the suspended matter in the Nile is highly ferruginous and this plays its part, doubtless, in the disappearance of nitrates and the purification of the water. The action of iron and its compounds in purifying waters is not understood, and deserves further study.

(g) The Nile is at its worst just before the flood, and at its best just afterwards. There is a second small rise in the coefficient of purity about the time when the flow of the Nile is checked by the opening of the irrigation canals and basins. (This will be further discussed in Part III.)

(h) The total solids and chlorin vary in inverse ratio to the height of the Nile, or in other words to its bulk.

This is almost a foregoing conclusion, as it is evident that a larger bulk moving at a quicker rate will not take up so large a percentage of impurity as a less quantity.

### III. THE CAIRO WATER COMPANY. NOTES ON THE WATER SUPPLY AND SANITATION OF EGYPT.

The Cairo Water Company draws its supply from the Nile just below the Kasr-el-Nil Barracks; the water is pumped to the filter beds at Abbasiyah, about three and a half miles; it flows first into a tank where a proportion of the suspended matter settles, and thence to the filter beds, which are composed of sand, fine, medium, and coarse gravel, and small stones, in layers of about thirty cm. each, the total thickness being 1.75 meters, and the filtered water is received in two covered reservoirs; from these it descends by gravitation to Cairo, about two miles off.

The company has a concession from the government expiring in 1913 for the sole supply of water, both filtered and unfiltered, to Cairo; the water is not required to be of any special purity, as long as it is *not worse than the Nile water*.

From time to time the *Bosphore Egyptien*, a Cairo journal, has complained of the quality of the water, and occasionally the government has ordered chemical investigations. The most important of these was carried out by Pappel and Legros in 1887, and in their report they condemned the water as bad, and recommended very radical changes in the beds of the company, including the construction of a tunnel of considerable length filled with broken

bricks, the increasing of the thickness of the filtering layer to 3.75 meters, and the building of a high wall to enclose the filter beds; they considered a settling tank not only useless, but rather injurious; no experiments were made beyond some half dozen determinations of free and albuminoid ammonia in the water and the sand of the filtered beds. This report was criticised very unfavorably by Tanquerel, of Cairo, and Muntz, of Paris, and the company brought forward certain facts in their defence which led the government to drop all inquiry.

By reason of the false position in which the government was placed, it was unable to get the water company to make any improvements, and the company became skeptical concerning scientific recommendations. In 1890 an outcry against the water was again raised, and the government took the matter up and entrusted the work to my hands.

I made analyses as follows:

	Water at intake.	Water in reservoir I.	Water in reservoir II.
Total solids.....	14.56	14.32	14.44
Loss on ignition .....	1.52	1.08	1.20
Oxygen absorbed, four hours..	0.268	0.140	0.177
Free ammonia .....	0.016	0.011	0.023
Albuminoid ammonia .....	0.039	0.009	0.011

As there was evidence of considerable purification, I reported to that effect, and refrained from offering unasked-for suggestions.

The attitude of the company became more favorable, and I believe they are quite willing to adopt any reasonable suggestions for the more efficient purification of the water. I am indebted to the kindness of the Director of the Cairo Water Company for aid in this research by the supply of sand for filtration.

TABLE XI. ANALYSES OF THE CAIRO WATER COMPANY'S WATER.

Date.	Total solids.	Suspended matter.	Chlorine.	Free ammonia.	Albuminoid ammonia.	Nitric acid.	O absorbed, 15 minutes.	O absorbed, 4 hours.	Coefficient of purity.	Coef of P. + Coef of P. of Nile water.
Mar. 25, 1891 .....	17.72	Trace	1.03	0.001	0.008	0.03	0.051	0.103	34.0	0.57
Apr. 23, 1891 .....	24.70	None	2.21	0.004	0.007	0.01	0.048	0.119	20.3	0.43
May 26, 1891 .....	20.76	"	3.14	0.001	0.009	0.08	0.064	0.189	41.3	0.58
June 29, 1891 .....	18.80	"	1.43	0.001	0.024	0.01	0.069	0.149	52.9	0.56
July 28, 1891 .....	18.60	Trace	0.91	Trace	0.009	0.13	0.057	0.080	29.0	0.60
Aug. 28, 1891 .....	17.24	"	1.02	0.001	0.007	0.05	0.053	0.082	26.2	0.61
Sept. 31, 1891 .....	14.12	"	0.79	0.001	0.005	0.08	0.045	0.092	23.8	0.67

In Table XI are given the results of the analyses of the water of the company made contemporaneously with those of the Nile at Cairo.

It is seen that the total solids and the chlorine remain almost the same as the quantities found in the Nile, the slight increase in the chlorine being due to the presence of small quantities of salt in the sand ; the coefficient of purity is, however, in all cases diminished about fifty per cent. The filters of the Cairo Water Company then do their work properly, and result in a purification of the Nile water. Judged by my scale, the water may be, except perhaps in June, considered good.

As the word "good" in water analysis is used somewhat loosely, and does not mean perfect, I instituted experiments in order to find out a better means of purifying the Nile water ; it is not necessary to detail the experiments, and I only give (in Table X) the figures of one of them. Four samples of the same water were examined.

(a) After precipitation of the suspended matter by a very small quantity of ferric chloride.

(b) After filtration as usual through double filters.

(c) After filtration through a layer of sand the same thickness as used by the Cairo Water Company.

(d) After filtration through a layer of fine sand 0.75 meter thick, a layer of "polarite" 0.20 meter thick, and a layer of coarse sand 0.75 meter thick.

From the results it is seen that filtration, even through paper (and its own suspended matter), improves the Nile water, doubtless assisted by the large surface exposed to the air ; filtration through sand improves it still more, and after filtration through "polarite" very little fault can be found with the water. The "polarite" in this case has exercised a reducing influence on the nitrates ; this is not always the case, and seems to take place when the "polarite" is fresh. In all my experiments the "polarite" purified the water to the extent of about eighty per cent., judged by my scale ; as to the exactness of this figure I cannot vouch, but it is certain that no other filtering material has given such satisfactory results in my hands. I therefore can strongly recommend the use of "polarite" to the Cairo Water Company. I may

mention that this material was handed to me with the simple description of "material for purifying water" and it was only after some difficulty that I established its identity. The monthly variations of the water of the company follow those of the Nile; the quality of the water in the river is dependent on the following:

(a) The (presumable) purity in the water of the Nyanzas and of the rainfall collected by the great watersheds of the White, the Blue, and the Black, Nile; (b) the taking up of impurities in the marshy districts of Central Africa; (c) the taking up of impurities during its flow, and the pollution of the river established at Cairo and more than probable at other points; (d) the self-purification of the river, in which the minerals in its bed and the suspended matter, probably aid the oxygen of the air. The quality of the Company's water is also dependent on (e) the filtering materials used.

The water at Port Said (*q. v.*) is analogous to the Cairo Water Company's water, as it is filtered at Ismalia before traversing the iron pipes which convey it to Port Said. The absence of nitrates at Port Said has already been explained.

My recommendation to the Cairo Water Company may profitably be extended to the other towns of Egypt; the Alexandria Water Company adopts a modification of Anderson's process, the short canal conveying the water from the Mahmoudieh Canal to their works being partly filled with scrap iron; my experiments showed me, however, that this method of purification was not so efficient as that by "polarite."

On looking over the results of the analysis of the water of the Bahr-Yousef, it has struck me that the apparent exception in July (see Table VII) may seem to contradict the conclusion I have drawn that the water of the Nile purifies itself during its flow; a glance at the conditions of the Bahr-Yousef will make it plain that this is but an apparent exception. In June the Nile is at its worst; it is directly afterwards flushed by the flood; as the Bahr-Yousef empties itself into the Birket-el-Kûm, which has no apparent outlet, a rapid flow of water cannot take place; the effect of the flood is to push down gradually the water that is in it. We should expect then to find the June bad water to occur at a later date in the Bahr-Yousef, and it is probably the bad water found

at Assiout in June, which makes the coefficient of purity high in July at Medinet-el-Fayoum. The same conditions obtain at Deyrout; this town is, however, much nearer Assiout, and has part of the water taken away by the Ibrahimieh Canal. I think that it would be correct to compare the water at Deyrout with that at Assiout a week beforehand, and that at Medinet-el-Fayoum with that a month before at Assiout. This should be noted in future researches.

#### IV. THE WATER OF THE NILE CHEMICALLY CONSIDERED AS THE SOURCE OF FERTILIZERS IN EGYPT.

In the preceding portions I have made no reference to the suspended matter. This I propose to do here.

The soil of Egypt is enriched by no artificial fertilizers, and the mud of the Nile is its only supply of those constituents which growing crops remove from the ground. Indeed, the soil of Egypt has been formed from the mud of the Nile by its deposition during the overflowing of its banks during past ages. I had first intended to study variations in composition of the mud, but soon finding that the laws governing the variations in the quantity of the suspended matter were very imperfectly understood, I relegated my first idea to the future, and devoted what time was at my disposal to the study of these laws.

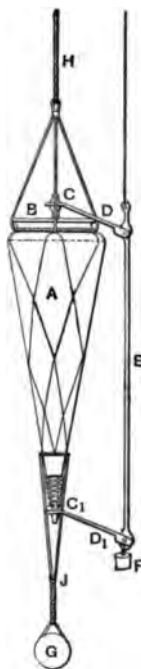
As the question of sampling was here very important I felt obliged to take the samples myself and had to devote a considerable time to traveling on the Nile for this purpose.

All samples were taken with the apparatus figured, which consisted of a funnel-shaped jar A closed at one end by a cork B to which was firmly riveted a metal plate one and a half mm. in thickness, and which was covered with sealing wax over its whole surface; through this cork, and soldered to the plate passed the tap C; at the other end the tap C<sub>1</sub> was fixed by means of a piece of India-rubber tubing, and held in place by being bound round with wire to two pieces of wood placed on each side; to the taps C and C<sub>1</sub> were fixed arms D and D<sub>1</sub>, which were connected by the rod E, weighted by the weight F; a cord was attached to the upper end of E, and by pulling this the two taps could be opened simultaneously, and on releasing it the weight F caused them to close; the whole apparatus was sus-



pended from the rope H by a net-work of cords which encircled the vessel A, and terminated in the rope J, from which hung the weight G; the capacity of the apparatus was two and a half liters.

It was used as follows: After being lowered to the required depth, the taps were opened by pulling the cord attached to E, the water entered by C<sub>1</sub>, and the air escaped by C; when no more bubbles of air could be seen rising, the cord was released, and the apparatus withdrawn; the water was then transferred to a bottle.



The shape of the apparatus was chosen in order to facilitate the escape of all the suspended matter in the bottle.

This apparatus was also used for sounding and measuring the difference of velocity between the surface and bottom of the river, as the bubbles practically always rose in a straight line. It was assumed that the difference between surface and bottom velocity was inappreciable.

Experiments were first made to determine whether the amount of suspended matter in different parts of the river was substantially the same or not.

In the first series samples were taken in the center of the river (a) at the surface, (b) at the bottom and (c) midway with the following results: Suspended matter, (a) 176.95; (b) 194.64; (c) 188.64.

In the second a mean sample was taken, (d) in the middle of the river, and (e) as near the banks as possible, with results as follows: Suspended matter, (d) 147.66; (e) 157.35.

The velocity was in both cases about four miles an hour.

These results showed that differences did exist in different parts of the river, but that they were not serious; except, perhaps, at the surface the difference does not exceed five per cent. All samples analyzed were mixtures of water from at least four different parts of the river, and may fairly be considered as average samples.

As the difference is shown to be small, the results in Tables

I, II, and III may be taken into consideration, and will be discussed later on.

In Table XII are given the results of the determinations of suspended matter in the water at Kasr-el-Nil at short intervals, together with the height of the Nile at Assouan, the approximate velocity deduced from the time taken by the water to flow from Assouan to Cairo (information supplied by the Chief Inspector of Irrigation), and the velocity at Kasr-el-Nil calculated from the amount of suspended matter by the formula given below.

In Table XIII are the results of analysis of corresponding samples of water at Assouan, Beni-Souef, Wasta, Atfeh, Helouan, and Kasr-el-Nil ; in Table XIV the results of analysis of corresponding samples at Assiout, Minieh, Beni-Souef, and Kasr-el-Nil ; and in Table XV the analysis of corresponding samples at Wady Halfa and Kasr-el-Nil. The samples at Wady Halfa and Assouan are not mean samples, but were taken at half a meter below the surface, and the results should therefore be increased by about five per cent., but this does not affect the conclusions drawn therefrom.

During one voyage up the Nile, I observed that at Maghagha the current at a certain part was only running at one and a half miles per hour ; at Manfalout finding a narrow creek, I ran my steam launch firmly aground, and by means of the propeller created an artificial current of ten miles an hour and a sample was taken after the lapse of some time ; these samples gave the following results on analysis :

Place.	Velocity.	Suspended matter.
Maghagha .....	1.5	21.72
Manfalout .....	10.0	953.6

From these I deduced the following formula, connecting the rate of flow and the amount of suspended matter,  $S = 9.5 V^2$  ; where S is the suspended matter in parts per 100,000, and V is the velocity in miles per hour.

By means of this formula, I have calculated the velocity of the Nile at Kasr-el-Nil on the 15th, 22nd, and 28th of August and the 4th and 15th of September, in each case with satisfactory results, considering the very approximate way of estimating the velocity, except on the 15th of August ; various consider-

ations, however, lead me to conclude that the velocity on that date at Kasr-el-Nil was greater than that stated, among which I may enumerate : (a) the river was rising very rapidly, there being an increase in four days of one meter, and it is highly probable that with such a rapid rise, a somewhat greater current should be obtained ; (b) under the Kasr-el-Nil bridge only a part of the river runs, there being another branch which conveys when the river is high, another part on the Guizeh side of Gezireh ; as the Nile was not very high on the 15th of August, it is probable that the bulk of the water traveled under the Kasr-el-Nil bridge, a comparatively narrow channel, and the actual velocity was by this slightly increased.

On the whole I think that the figures in Table XII confirm the formula.

It is necessary, in order that the formula hold that the following premises be granted : (a) that the density and surface tension of the mud (and therefore the size of particles) be constant ; (b) that the water be mixed throughout ; (c) that the water be saturated with mud.

Considering that the composition of the mud is, within very narrow limits, constant, premise (a) may be assumed to be correct ; of the practical correctness of the other two, my personal observations during my voyages on the Nile during its flood, have convinced me ; I noted especially the numerous currents and cross currents, the destruction of the banks, and their rapid absorption, the practical absence of much mud at the bottom of the river, and sundry smaller points.

The truth of the premises is indirectly confirmed by the agreement between the numbers found and calculated in Table XII.

TABLE XII. DETERMINATIONS OF SUSPENDED MATTER AT KASR-EL-NIL (CAIRO).

Date.	Height of Nile at Assouan.	Approximate velocity.	Suspended matter.	Calculated velocity.
August 1, 1891 .....	87.35	2.5	29.80	....
" 11, 1891 .....	90.44	3.85	98.48	....
" 15, 1891 .....	91.43	3.85	188.64	4.46
" 22, 1891 .....	92.24	3.85	134.30	3.78
" 28, 1891 .....	92.44	3.85	160.44	4.09
September 4, 1891 .....	92.61	3.85	147.66	3.94
" 15, 1891 .....	92.87	3.85	151.64	3.99

I have also frequently observed that when the Nile mud is allowed to settle, it cakes after a lapse of time, and becomes difficult to remix with the water until after a certain amount of force has been used to stir it up ; after being stirred up it is easy of absorption by the water until allowed to cake again.

On these observations I have founded the following theory ; The suspended matter is brought down by the Blue Nile and the Atbara (and to a lesser extent by the White Nile), and has little tendency to deposit until the flow is checked ; this check occurs first and principally in Lower and Middle Egypt by the drawing off of the water into the canals and basins for the irrigation of the country, and it is there that the mud is principally deposited ; there is little tendency to deposit in Upper Egypt and farther south, as the velocity is to a much greater extent maintained during the depositing period ; the mud-carrying waters of the Blue Nile and the Atbara, having been diluted by the comparatively clear waters of the White Nile, the river is probably by no means saturated, and cannot become so in Upper Egypt and above during the flood, as there is no great store of deposited mud ; the deposited mud remains at the bottom and sides of the river during the period of low Nile and consequently low velocity, and cakes, thereby becoming a mass requiring a certain force given by a certain velocity (probably exceeding three miles an hour), to re-absorb it, and the water cannot become saturated till this "critical velocity," has been attained. On the attainment a rapid increase in the amount of suspended matter takes place in Middle and Lower Egypt until saturation is attained.

According to this theory the quantity of suspended matter should be, during flood time, actually greater in middle and Lower Egypt than in Upper Egypt ; the correctness of the theory is borne out by the results in Tables XIII and XV, where it is shown that the Nile at Assouan and Wady Halfa contains considerably less suspended matter than the water at Cairo.

TABLE XII. SUSPENDED MATTER AT ASSOUAN, BENI-SOUËF, WASTA, ATFEH, HELOUAN, AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
August 16, 1891 .....	Assouan	92.15	104.90
" 27, 1891 .....	Beni-Souef	92.21	141.83
" 22, 1891 .....	Wasta	92.21	139.50

TABLE XIII. SUSPENDED MATTER AT ASSOUAN, BENI-SOUËF, WASTA, ATFEH, HELOUAN, AND CAIRO. (CONTINUED.)

Date	Place.	Height of Nile.	Suspended matter.
August 22, 1891.....	Atfeh	92.21	147.23
" 22, 1891.....	Helouan	92.21	143.59
" 22, 1891.....	Kasr-el-Nil	92.21	134.20

TABLE XIV. SUSPENDED MATTER AT ASSIOUT, MINIEH, BENI-SOUËF, AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
September 13, 1891.....	Assiout	92.87	149.82
" 14, 1891.....	Minieh	92.87	152.20
" 14, 1891.....	Beni-Souef	92.87	147.32
" 15, 1891.....	Kasr-el-Nil	92.87	151.67

TABLE XV. SUSPENDED MATTER AT WADY HALFA AND CAIRO.

Date.	Place.	Height of Nile.	Suspended matter.
August 15, 1891.....	Wady Halfa	92.44	112.10
" 28, 1891.....	Kasr-el-Nil	92.44	160.44

The results in Tables XIII and XIV show that the suspended matter is practically constant below Assiout, as is also the velocity; the water then is saturated here (*i. e.*, in Middle and Lower Egypt).

On the 1st and 11th of August, for which dates I have not calculated the velocity by the formula, the "critical velocity" had probably not been attained, and the water had not become saturated; premise (c) then does not hold, and therefore the formula would not be applicable.

My theory also explains the sudden increase of the suspended matter and its more gradual fall.

Although the suspended matter has its origin in the Blue Nile and Atbara (for the most part) the actual quantity in the Nile in Middle and Lower Egypt during flood time depends not on the amounts in these rivers, but on the velocity of the current.

Considering that my theory explains all the points concerning the amount of suspended matter in the Nile, it may be taken as generally true. The amount of suspended matter has no direct relation to the height of the Nile, but is dependent on the velocity, and it is a matter of extreme regret that I did not realize this at the time of making my experiments, or I should

have devoted my attention to the accurate determination of the velocity.

Dredgings were made of the bed of the river at Assiout, Minieh, Beni-Souef, Wasta, Atfeh, Bedrishen, old Helouan, Dar-el-Tin, Rodah, Guizeh, Guizeh Palace, and Kasr-el-Nil during the flood, and in each case the bed was found to consist chiefly of sand, with about five per cent. of mud and small quantities of the magnetic oxid of iron mentioned above; samples were also taken just below the water and from the top of a small sand island formed by the Nile opposite Katr-el-Nabi, which had the same composition; the formation of this island, and the presence in the sand as low as Cairo of the heavy magnetic oxid of iron, which occurs above Assiout, are striking examples of the force of the current.

I have made no detailed experiments on the variations of the composition of the mud; the constituents valuable to agriculture are however practically constant in amount, and my conclusions as to the supply of mud may be taken as generally true as to the supply of fertilizers.

(V.) NOTES ON THE AGRICULTURE AND IRRIGATION  
OF EGYPT.

Egyptian agriculture is the mainstay of the country's prosperity, and the Nile is the mainstay of the agriculture. Fertilizers, as such, are not placed on the land, and the soil is dependent for its supply of the constituents annually removed by the plants in the mud brought and deposited by the Nile water. In former days the Nile was simply allowed to overflow its banks and inundate the country, the mud settled, and when the Nile fell again the clear water (mostly) drained off; this system is still followed in Upper Egypt, but in the remaining country the banks of the Nile have been raised and the water flows into canals, whence by a series of ramifications the water is allowed to pass on to the land. Looked at solely by the light of my theory the canal system is inferior to the older one, owing to the abundant opportunity for deposition of mud owing to the decreased velocity in the canals, and *the probable non-attainment of the "critical velocity"* in a very considerable portion of them

This non-attainment of the "critical velocity" has a considerable importance. The Nile bed is annually cleared out by the flow of the river, the canal beds are not, and therefore they are steadily rising and helping to diminish the supply of water, and therefore fertilizers to the land. Another difficulty is being felt; the level of the land is also rising, as it receives a slight addition yearly, and in lapse of time, it must be and in some cases is, too high for the proper flow of the water thereon. The Barrage was established in order to raise the height of the Nile, and to grapple with this difficulty. The difficulty is now again felt, and the proposals to grapple with it generally take the form of raising the height of the Nile by similar artificial structures. It is absolutely necessary not to lose sight of the fact that it is not large quantities of water that the land requires; it is the mud contained in them, and the primary object, the amelioration of agriculture, will be defeated, if, although a much larger supply of water be given to the land, this water contains less mud.

In raising the height of the Nile, nothing must be done to in any part check its velocity, and attention must be paid to keeping up this velocity to the greatest possible extent in the canals; it is better to be content with a much smaller quantity of water if it can be supplied with a great velocity, than to so raise the Nile as to allow enormous quantities of water to flow on the land at a very slow speed; it is necessary to keep up the "critical velocity" in order to make the mud deposited during the period of slow velocity available at the necessary time.

I fully realize that there are enormous engineering difficulties, but at the same time my study of the Nile has revealed to me these points which are not fully realized; it is beyond the scope of a chemist to discuss this question in more detail.

Wilcox's book on the irrigation system of Egypt gives very complete information on the engineering work of Egyptian irrigation.

#### (VI.) CONCLUSIONS AND SUGGESTIONS.

The conclusions from my work on the Nile are:

- (1) The impurities in the Nile water are influenced by (a) the White Nile and analogous tributaries; (b) the Blue

Nile and analogous tributaries ; (c) the impurities taken up during its flow ; (d) the self-purification it undergoes, of which (d) is the most important.

- (2) The water of the Nile, at Cairo, is a moderate drinking water, and not an excessively bad one, as has been maintained : after filtration through sand, as practised by the Cairo Water Company, not much exception can be taken to it. The Cairo Water Company's supply is, on the whole, good.
- (3) After filtration through "polarite" it becomes a most excellent drinking water, fully equal and in many cases superior to the water supplied to great English towns.
- (4) The Nile in its downward flow takes up impurities both mineral and those due to sewage ; these are, however, insignificant when compared with the great bulk of water and to the self-purification.
- (5) The amount of nitric acid is remarkably small.
- (6) The purification and deficiency of nitric acid are largely due to the iron minerals in its bed (*e. g.*, magnetic oxid of iron, ferrous silicate, etc.).
- (7) The quality of the water is worst just before the annual rise, and at its best just after the attainment of its maximum
- (8) The suspended matter, which supplies the fertilizers necessary to the agriculture of the country, is not only dependent on the quantity brought down by the Blue Nile, etc., but also and more especially on the velocity of the river.
- (9) Portions of the suspended matter become deposited on the bed of the river, as the current slackens, and a certain "critical velocity" is necessary to stir this up again, so as to be again taken into suspension.
- (10) After the "critical velocity" has been attained, the water saturated with mud, the relation between suspended matter (S) and velocity (V) is expressed by the formula  $S = 9.5V^2$ .
- (11) After the water is saturated (which only occurs in Middle and Lower Egypt) the quantity of suspended matter is greater than that found in the Nile in Upper Egypt and above.



- (12) Any diminution of the current of the river, and especially the prevention of the attainment of the "critical velocity" at the proper time will cause a loss of suspended matter and therefore a detriment to agriculture.

I can only look upon my work as preliminary to a thorough investigation of the Nile in the future; there are many points to be determined (*e. g.*, the "critical velocity," the actual amount of fertilizers necessary, and the lowest safe velocity, the laws that govern the settling of the mud, and the purification of the water, the composition of both water and mud, and the part played by each constituent) and these I leave as a legacy to my successors.

As Egypt depends on the Nile, it is imperative for the Egyptian government to have the fullest information on the Nile at their disposal, in order to control the river so as to obtain the greatest possible benefit therefrom. My work was chiefly done at the Khedivial Laboratory, at Cairo, but I found that the rough laboratory that I fitted up on board the steam launch, No. 74, was of great assistance, and future investigation should be carried on in a laboratory of this description; it would require a steamer large enough to hold thirteen or fourteen persons, and powerful enough to steam six miles against the full stream, and of low draught,—preferably a stern-wheeler.

At least five years should be devoted to the work, and the total expenses would be:

Initial expenses.....	£1650
Five years, at £1903.....	9515
Total.....	£11,165

The Egyptian government should be prepared to find that sum. A great deal of work could also be done on the minerals of Egypt at the same time.

My conclusion (12) is highly important to the irrigation service, and I recommend it to the notice of the Public Works Department.

This paper contains the substance of a report made by me to the Director of the Sanitary Administration.

In conclusion I must express my warmest and most grateful

thanks to Dr. Hussein Off, third chemist in the Khedivial Laboratory, for his aid; the devoted way in which he worked with me, often far into the small hours of the morning, has contributed greatly to the completion of my work.

### ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND J. BIRD MOYER.

In a former communication we demonstrated by a sufficient number of carefully made experiments that mercury and bismuth could not be separated electrolytically in a nitric acid solution. This was in line with the observations of Smith and Saltar,<sup>1</sup> who proved conclusively that copper and bismuth could not be separated under analogous conditions, and further that the statement in regard to the separation of bismuth and lead was incorrect. Pursuing our original intention of studying the electrolysis of metals in the presence of free nitric acid, we offer the following additional experience in this field of investigation. We naturally expected little trouble, and indeed met with very little in our efforts to separate

#### *Mercury from Lead.*

1. Ten cc. of mercuric nitrate solution ( $=0.1150$  gram of metallic mercury), one cc. of lead nitrate solution ( $=0.0126$  gram of lead dioxide), and twenty-five cc. of nitric acid of sp. gr. 1.3, were diluted to 175 cc. and electrolyzed with a current liberating 1.3 cc. of electrolytic gas per minute. The precipitated mercury weighed 0.1151 gram, and the lead dioxide equaled 0.0123 gram. An examination of the mercury did not reveal any admixed lead.

2. In this experiment the quantities of lead and mercury were the same as in 1; the volume of nitric acid was increased to thirty cc. while the current registered 1.8 cc. of electrolytic gas per minute. The mercury deposit weighed 0.1150 gram and the dioxide of lead equaled 0.0126 gram.

In three other experiments in which the volumes of the added nitric acid (sp. gr. 1.3) equaled five cc., ten cc., and fifteen cc., respectively, the precipitated mercury contained metallic lead in varying but very considerable amounts.

<sup>1</sup>J. Anal. Appl. Chem., 7, 128.

*Mercury from Lead and Bismuth.*

In our former communication we cited an outlined analysis of an alloy containing tin, mercury, lead, and bismuth, by Classen in his *Quantitative Analyse durch Elektrolyse, dritte Auflage*, p. 147, and showed that if it were conducted as there directed the analyst would in the end have little bismuth to determine as it would have most certainly gone out in company with the mercury. Omitting tin, we subjected a nitric acid solution of the other three metals to the action of the current. The solution contained 0.1150 gram of mercury, lead equal to 0.0126 gram of dioxide, bismuth 0.0718 gram, and fifteen cc. of nitric acid (sp. gr. 1.3). The total dilution was 180 cc. The current liberated 1.7 cc. of electrolytic gas per minute. The deposited mercury weighed 0.1262 gram and the increase in weight of the anode was 0.0164 gram; bismuth was discovered at both poles. A second and a third experiment with increased volume of acid resulted similarly. We must, therefore, reject this course if a satisfactory separation is desired.

*Silver from Lead.*

The separation presented no particular difficulties when working with conditions analogous to those recorded in the two following experiments:

1. Ten cc. of silver nitrate solution (= 0.1028 gram of silver), one cc. of lead nitrate solution (= 0.0144 gram lead dioxide), and fifteen cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc., were acted upon by a current generating 1.8 cc. of electrolytic gas per minute. The deposit of silver weighed 0.1023 gram, and the lead dioxide 0.0145 gram.

2. The conditions were similar to those in 1. The precipitated silver weighed 0.1028 gram, and the lead dioxide 0.0145 gram.

*Copper from Cadmium.*

This separation was long since satisfactorily made by Smith. Classen met with similar results (*Berichte*, 17, 2473). Those interested will find Smith's description of the method fully given in the *American Chemical Journal*, 2, 41. The results

we append confirm those obtained by Smith in every particular.

1. Ten cc. of a copper sulphate solution ( $= 0.1341$  gram of copper), five cc. of cadmium nitrate solution ( $= 0.1$  gram of cadmium), and five cc. of nitric acid (sp. gr. 1.2), with total dilution of 200 cc., were electrolyzed with a current that gave 0.6 cc. of electrolytic gas per minute. The precipitated copper weighed 0.1346 gram; it contained no cadmium.

2. With conditions similar to those in 1, the precipitated copper weighed 0.1341 gram. The current gave 0.6 cc. of electrolytic gas per minute.

*Copper from Zinc.*

The quantities of metal were equal; the volume of nitric acid was five cc. (sp. gr. 1.3), total dilution 200 cc., and the current gave one cc. of electrolytic gas per minute. The precipitated copper weighed 0.1345 gram instead of 0.1341.

*Copper from Zinc, Cobalt, and Nickel.*

The quantities of metal were equal; the volume of nitric acid (sp. gr. 1.3) was five cc. and the total dilution 200 cc. The current registered 0.4 cc. of electrolytic gas per minute. The precipitated copper weighed 0.1339 gram.

*Copper from Iron and Zinc.*

The metals were equal in quantity. The volume of nitric acid was five cc. (sp. gr. 1.3). The current gave 0.7 cc. of electrolytic gas per minute, while the dilution was the same as in the preceding separations. The metal deposit weighed 0.1340 gram.

The copper obtained in each of these separations was examined for the metals associated with it in solution, but they were not found present. We may say here that we claim nothing new in these separations of copper from zinc, nickel, cobalt, and iron. They have been performed by others, but we merely offer our results and the conditions under which they were obtained as guides for any who may have occasion to make such separations.

*Bismuth from Cadmium.*

1. Five cc. of bismuth nitrate solution ( $= 0.0718$  gram of metallic bismuth), five cc. of cadmium nitrate solution ( $= 0.1$

gram of cadmium), and fifteen cc. of nitric acid (sp. gr. 1.1) were diluted to 180 cc. and electrolyzed with a current liberating 1.6 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0716 gram instead of 0.0718 gram.

2. The conditions in this experiment were analogous to those in 1, except that no additional acid was added to the nitric acid solution of the two metals. The precipitation bismuth weighed 0.0719 gram.

*Bismuth from Zinc.*

0.0718 gram of bismuth, 0.1 gram zinc in the presence of two cc. of nitric acid (sp. gr. 1.3), with total dilution of 200 cc. gave 0.0712 gram of bismuth to a current setting free 0.4 cc. of electrolytic gas per minute. The anode was slightly discolored; its increase in weight was 0.0003 gram.

In a second trial with 1 cc. of additional acid the precipitated bismuth weighed 0.0717 gram. We can therefore regard this separation as satisfactory.

*Bismuth from Nickel.*

1. 0.0718 gram of bismuth, 0.1 gram of nickel, in the presence of two cc. of nitric acid (sp. gr. 1.3), were diluted to 180 cc. with water. A current liberating 0.5 cc. of electrolytic gas per minute acted upon this solution. The precipitation of bismuth was complete; the metal deposit weighed 0.0724 gram.

2. In this trial the quantities of the metals equaled those given in 1; the total dilution was 200 cc.; the volume of nitric acid of sp. gr. 1.3 equaled three cc. and the current gave 0.2 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0716 gram.

A third experiment with conditions exactly like those of 2 gave 0.0716 gram of bismuth. The latter contained no nickel, and there was no deposit upon the anode.

*Bismuth from Cobalt.*

The quantities of metal were 0.0718 gram of bismuth and 0.1 gram of cobalt; the nitric acid (sp. gr. 1.3) equaled three cc., and the current gave 0.2 cc. of electrolytic gas per minute. The deposit of metallic bismuth weighed 0.0714 gram and there was also a very slight discoloration of the anode.

Other trials showed that the separation was possible.

It may be of interest to show what results were obtained when mixtures of the preceding metals were electrolyzed.

*Bismuth from Zinc, Cobalt, and Nickel.*

1. 0.0718 gram of bismuth, 0.1 gram of zinc, 0.1 gram of cobalt, and 0.1 gram of nickel were mixed with two cc. of nitric acid (sp. gr. 1.3), diluted to 200 cc., and acted upon by a current liberating 0.8 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0739 gram, and upon examination showed the presence of both nickel and cobalt. The anode was covered with a blue coating.

A second, third, and fourth trial, with conditions almost identical with those in the preceding example, showed the presence of 0.0729 gram, 0.0738 gram, and 0.0739 gram of bismuth, which in each instance was contaminated with cobalt and nickel.

*Bismuth from Cobalt and Nickel.*

Zinc was omitted, and by employing the remaining three metals in the amounts given in the preceding experiment, using three cc. of nitric acid of sp. gr. 1.3, and acting upon the mixture after dilution to 200 cc. with a current liberating 0.3 cc. of electrolytic gas per minute, the bismuth that was precipitated weighed 0.0736 gram. It contained nickel.

*Bismuth from Cobalt and Zinc.*

0.0718 gram of bismuth and 0.1 gram each of cobalt and zinc were mixed with two cc. of nitric acid of sp. gr. 1.3, diluted to 180 cc. with water, and electrolyzed with a current giving 0.6 cc. of electrolytic gas per minute. The bismuth weighed 0.0747 gram; it contained cobalt, and the anode was covered with a film of oxide.

*Bismuth from Cobalt, Nickel, and Zinc.*

Using the same quantities of metals as given in the preceding experiments we increased the volume of added acid to five cc. The deposit of bismuth weighed 0.0728 gram and contained both cobalt and nickel.

Upon making a trial with the following conditions we were successful in effecting the separation with all the metals present: 0.0718 gram bismuth, 0.1 gram zinc, 0.1 gram cobalt, 0.1 gram

nickel, eight cc. of nitric acid of sp. gr. 1.3, total dilution 200 cc., and a current that gave 0.4 cc. of electrolytic gas per minute. The deposit of bismuth weighed 0.0718 gram. It did not show the presence of any other metal upon examination. In this separation there was no discoloration of the anode. Subsequent experiments were equally successful in the separation, although in several of them the anode was slightly discolored; its weight, however, was not increased more than 0.0004 gram.

We may add that the bismuth was deposited upon platinum dishes weighing from sixty to seventy grams. The metal deposit was, in all those trials that approached success, adherent and regular in appearance. It was washed with warm water, alcohol, and ether. The strength of current indicated in all the experiments given in this communication were with voltmeter and electrolyte in circuit.

While the separation of bismuth from the various metals mentioned is possible if the conditions we have worked out are preserved, we cannot fail to observe that the solution in nitric acid is not nearly so satisfactory as that in which the metals exist as sulphates together with free sulphuric acid. With this last solution Smith and Knerr<sup>1</sup> obtained very excellent results.

CHEMICAL LABORATORY OF  
THE UNIVERSITY OF PENNSYLVANIA,  
APRIL 27, 1893.

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## THE WORLD'S CONGRESS AUXILIARY OF THE WORLD'S COLUMBIAN EXPOSITION.

[DEPARTMENT OF SCIENCE AND PHILOSOPHY. GENERAL DIVISION OF CHEMISTRY].

THE committees in charge of the congress have selected Monday, August 21, as the date of the opening of the congress of chemists to be held in connection with the Columbian Exposition, in Chicago.

The chairman of the committee appointed for co-operation in this congress by the American Association for the Advancement of Science, Chemical Section, is Prof. Ira Remsen, Johns Hopkins University, Baltimore, Md. The chairman of the committee appointed by the American Chemical Society is Dr. Wm.

<sup>1</sup> *Am. Chem. J.*, 8, 206.

McMurtrie, 106 Wall street, New York, N. Y. The chairman of the committee of the World's Congress Auxiliary, on Congress of Chemists, is Prof. John H. Long, 2421 Dearborn street, Chicago, Ill. The various committees have organized by selecting Dr. H. W. Wiley, chief chemist of the Department of Agriculture, Washington, D. C., as chairman, and Prof. R. B. Warder, Howard University, Washington, D. C., as secretary.

The work of the congress has been divided into ten sections and a temporary chairman has been selected for each section, as follows :

Agricultural Chemistry, H. W. Wiley, Department of Agriculture, Washington, D. C.; Analytical Chemistry, A. B. Prescott, Michigan University, Ann Arbor, Mich.; Didactic Chemistry, W. E. Stone, Lafayette, Ind.; Historical Chemistry and Bibliography, H. C. Bolton, University Club, New York; Inorganic Chemistry, F. W. Clarke, Geological Survey, Washington, D. C.; Organic Chemistry, I. Remsen, Johns Hopkins University, Baltimore, Md.; Physical Chemistry, R. B. Warder, Howard University, Washington, D. C.; Physiological Chemistry, V. C. Vaughan, Michigan University, Ann Arbor, Mich.; Sanitary Chemistry, H. Leffmann, 715 Walnut street, Philadelphia, Pa.; Technical Chemistry, Wm. McMurtrie, 106 Wall street, New York, N. Y.

General and special invitations have already been issued to foreign chemists and many replies have been received, indicating a large attendance of chemists from abroad at the congress.

The following distinguished foreign chemists have already promised to present papers to the congress and the list will without doubt be increased many fold before the date of the opening :

Prof. L. G. N. Ernest Milliau, Marseilles, "On Standard Methods of Oil Analysis;" Mr. Farnham Maxwell Lyte, London, "On the Production of Chlorine;" Mr. H. Droop Richmond, London, "On the Accuracy of the Methods of Analyses of Dairy Products;" Mr. Pierre Manhes, Lyon, subject to be announced later; Prof. B. Tollens, Göttingen, "Researches on the Synthesis of Polyatomic Alcohols;" Prof. Ferd. Tiemann, Berlin, subject to be announced later; Mr. H. Pellet, Brussels, "On the Methods of Determining the Percentage of Sugar in Beets;" Mr. H. R. Procter, Leeds, "On the Examination of Tanning Materials;" Mr. O. Kemna, Antwerp, "On the Purification of Water;" Mr. Otto Hehner, London, subject to be announced; Prof. C. A. Bischoff, Riga, subject to be announced; Prof. G. Lunge, Zürich, "On the Method of Teaching Technological Chemistry at Universities and Polytechnic Schools;" Prof. Ludwig Mond, Rome, subject to be announced; Prof. W. N. Hartley, Dublin, subject to be announced; Prof. R. Biedermann, "The Influence of Potent Laws on the Development of Chemistry."

This circular is especially intended to reach American chemists,



inviting them to take an active interest in the congress and to be present, or if that is not possible to send papers on some of the subjects indicated in the classification above mentioned.

Chemists specially interested in each of the subjects for discussion are invited to correspond with the chairmen of those sections in regard to the character of the work and of the papers expected. All chemists who expect to read papers at the congress are earnestly requested to send the titles thereof to the chairman of the General Committee, Dr. H. W. Wiley, Department of Agriculture, Washington, D. C., on or before the first day of August. It will be difficult to arrange for a position on the program for the titles of any papers which may be received after that date. The time required for each paper should also be noted so that daily programs can be provided for in advance. In all cases the place of honor on the program will be given to foreign contributors. Papers or addresses can be presented in English, French, or German as the author may select, but where convenient the English language will be preferred.

The committee desires to ask those chemists who propose to attend the World's Congress to make an excursion during the week previous to the meeting to Madison, Wis., for the purpose of attending the meetings of the Chemical Section of the American Association for the Advancement of Science. This will not only be a delightful excursion, as Madison is distant only about four hours from Chicago, but will also enable the participants in the congress to make the acquaintance of the scientific men of the United States and other countries, engaged not only in chemical, but also in other branches of science.

Other attractions in Chicago will be meetings of different chemical societies. Among these may be mentioned the American Chemical Society, the annual meeting of which will begin August 21, and the Association of Official Agricultural Chemists, which will hold its annual meeting in Chicago, beginning Thursday, August 24. The sessions of these societies will be so ordered as not to conflict with the business of the congress. The American Pharmaceutical Association, which has a strong chemical section, will also meet in Chicago at or near this time. The American Institute of Mining Engineers will also hold its

meeting in Chicago beginning on Monday, July 31. It is thus seen that this occasion will bring together the active workers in all branches of chemical science in the United States and enable American chemists to make the acquaintance of distinguished co-laborers from abroad, and the visiting chemists to meet the largest possible number of their fellow-laborers here.

Every possible arrangement will be made for the convenience and comfort of visitors. Intending participants in the congress should address Prof. John H. Long, 2421 Dearborn street, Chicago, Ill., for information in regard to quarters and other accommodations. On arrival in Chicago, visitors should report at once to the Congress Headquarters, Art Institute Building, Lake Front and Adams Street, where full information will be given them in regard to matters connected with their personal comfort. Wherever possible, intending visitors should write a few days before their arrival to the address above mentioned in order that special provision may be made for their comfort when they reach Chicago.

In regard to the climate of Chicago in August much can be said in praise. While warm days may sometimes be expected the situation of the city on the edge of a vast open prairie extending for nearly a thousand miles north and west without a break secures even in the hottest day refreshing breezes which cool the atmosphere and mitigate the heat of summer. The lake breezes also do much to render the climate moderate. No one need be deterred from attending the congress on account of fear of severe heat.

It is especially urged that all chemists who intend visiting the World's Fair take this occasion to do so, by which they can combine the pleasure of visiting the Exposition with the benefit derived from attendance at the congress. To American chemists an especial appeal is made to be present for the purpose of welcoming our foreign visitors and showing them the progress of chemical science in the United States.

HARVEY W. WILEY,

Chief of Chemical Division, U. S. Department of  
Agriculture, and Chairman of the Joint Com-  
mittees on the World's Chemical Congress.

## MUTER'S METHOD FOR THE ANALYSIS OF FATS AND OILS.<sup>1</sup>

BY NATHANIEL J. LANE.

In the *Analyst* of April, 1889, Muter publishes a method of analyzing fats and oils, which consists in determining the percentage of fluid acids and their iodine absorption.

The method is as follows :

It is first necessary to describe "Muter's Olein Tube." This is essentially a burette with a bulb at the top, and provided with a well-ground stopper. The graduated part is of such a width as to show distinctly one cc. in the graduations, and it has a stop-cock at a height of fifty cc. from the bottom. The graduations commence at forty cc. from the lower end, and continue up to 250 cc., ending just below the bulb. The tube can be fastened in an ordinary clamp, and may be arranged in a water-jacket in warm weather.

### THE PROCESS.

Weigh off about three grams of the oil or fat in a tared flask ; an Erlenmeyer of about 200 cc. capacity is convenient. To this add fifty cc. alcohol and a fragment of solid potassium hydrate sufficiently large to saponify the fat. Close the mouth of the flask with a cork carrying a long tube drawn to a point, and heat on a water-bath until completely saponified ; add a drop of phenolphthalein and then acetic acid to faintly acid reaction and drop in alcoholic potash until the very *slightest* pink tinge is restored. 200 cc. of boiling distilled water are placed in a 500 cc. basin, thirty cc. of a ten per cent. solution of lead acetate are added and the whole boiled. Into this the soap solution is slowly poured, with constant stirring, and the whole allowed to cool slowly stirring well so as to cause the precipitate to agglomerate, and the clear liquor is poured off. Boiling water is poured on, and the precipitate washed by decantation, working rapidly. When the washing is complete, the precipitate is scraped from the basin into a stoppered bottle, and eighty cc. of *redistilled*

<sup>1</sup> Read before the New York Local Section, June 2, 1893.

ether<sup>1</sup> having been poured on it, the remaining particles of the precipitate are washed from the basin into the bottle with ether, and the bulk of ether in the bottle is made up to 120 cc. The bottle is securely closed and allowed to stand (with occasional shaking), for twelve hours, during which time the lead oleate will entirely dissolve. A funnel with a ground edge is arranged over the "olein tube," a filter is placed therein and the contents of the bottle having been filtered into the tube, the insoluble lead stearate, etc., remaining on the filter, is washed with ether until the washings pass free from lead. This will usually be attained by the use of 100 cc. of ether; during the filtration and washing the funnel must be kept covered by a ground glass plate. The funnel having been removed, dilute hydrochloric acid is poured into the tube up to the first mark (thus using about forty cc. of acid, one in four) and the tube having been closed by the stopper and taken from the clamp, is thoroughly shaken until the decomposition is complete, which is indicated by the ethereal solution clearing up. The tube is returned to the clamp, the liquids allowed to separate, and the aqueous layer is run off by the bottom pinch-cock. Water is then poured in up to the same mark, the whole is again shaken and separated as before, and this is repeated until the washings are drawn off free from acidity. Water is then once more run in until the ether is forced up to the zero mark, and ether added (if necessary) so as to bring its upper layer to a definite point (say 200 cc.), and the total volume is read off and noted. Fifty cc. of the ethereal solution of the fluid acids are run into an Erlenmeyer flask, and the flask having been attached to a condenser, the ether is distilled off by a bath of warm water until only a little remains. It is important that the whole of the ether should not be distilled off, so as to avoid contact of the acids with the air. Fifty cc. of pure alcohol (or methylated spirit that has been rectified over potassium hydrate) are added to this residue, and the solution is titrated with decinormal soda,

<sup>1</sup> Since reading this paper, I have noticed an article in the *Analyst* of December, 1892, by Otto Hehner on the separation of solid and liquid acids, in which he says that the accurate separation of the above acids by solution in ether is impossible, owing to the solubility of lead stearate in ether, but as he extracted in a Soxhlet, the ether was, of course more or less warm and I have found that the hot ethereal solution invariably holds up lead salts of solid acids, which are deposited on cooling.

using phenolphthalein as indicator. Each cc. of soda used represents 0.0282 of oleic acid, and the amount found is calculated up to the total bulk of the ethereal solution, so as to obtain the total liquid acids in the weight of fat started with.

Run off as many cc. as will contain 0.5 gram of oleic acid (or as nearly that quantity as can be conveniently measured by the instrument, of course carefully noting the amount taken) into a stoppered bottle, of at least 350 cc. capacity the ether distilled off in a current of carbonic acid, which has been passed through a solution of sodium bicarbonate and dried over calcium chloride, and when *every trace* of ether has been expelled, fifty cc. of Hubl's solution are added, set aside in a perfectly dark place, with a blank and after twelve hours titrated as usual.

While the results obtained by this process were unexceptionable, it was too tedious for factory work; therefore experiments were made to shorten it, which resulted in the following modification: Precipitate the lead soaps in a 600 cc. Erlenmeyer flask, in place of a basin, cool under running water, giving the flask a circular motion, which causes the precipitate to adhere to the sides; when the flask is perfectly cold wash by decantation, using hot water, and rinse once with alcohol, then add 120 cc. of ether (redistilled), attach a reflex condenser, and boil on a water-bath until all the lead oleate is dissolved and the insoluble portion is a fine powder. Then cool *thoroughly*; this is very important, as some of the lead compounds are soluble in hot ether, but not in cold. The object of boiling the lead soaps with ether is to shorten the filtration, for when treated as Mutter directs, the filtration takes six to eight hours, while boiling reduces the time from twenty-five to fifty minutes. The balance of the process is carried out exactly as Mutter directs.

The following are some results obtained by the process :

	Sample number,				
	570	571	572	573	574
Liquid acids.....	68.05	75.16	77.64	76.73	76.67
" " iodine number	141.09	141.96	143.49	141.97	140.59
Hubl's number .....	99.30	108.36	110.96	108.95	109.229
Saponification equivalent .	288.21	297.51	296.27	284.75	288.94
Titer of fatty acids.....	36.6	32.4	30.4	33.8	33.40

No. 570 is Cotton Seed Stearine, one year old.

" 571 is Summer Yellow C. S. oil, one year old.

" 572 is Winter Yellow C. S. oil, one year old.

" 573 is C. S. oil from Columbia, S. C.

" 574 is C. S. oil from New Orleans.

	575	Sample number.	
		1529	1530
Liquid acids.....	64.15	83.97	86.96
" " iodine number	99.48	144.40	139.40
Hubl's number.....	64.96	121.70	122.70
Saponification equivalent.	287.85	.....	.....
Titer of fatty acids .....	37.4	.....	.....

No. 575 is an average sample of Steam Lard.

" 1529 is Corn Oil.

" 1530 is " "

" 1626 is Peanut Oil: the solid fatty acids showed Arachidic acid in large quantity.

The iodine number of the liquid lard acids is unusually high; Muter gives ninety-two to ninety-four, but this seems rather too low, the average being about ninety-six. I hope, at some future period to make a more complete investigation of this method, and present the results to the Society.

### LABORATORY NOTES.

BY FRANK JULIAN.

Received June 22, 1893.

#### DETERMINATION OF CARBON IN STEEL.

**A**FTER dissolving a sample of wrought steel in copper-ammonium-chloride or copper-potassium-chloride, the carbon remains in the form of a soft mass, which is tedious to filter and troublesome to wash completely. These difficulties may be overcome by the use of the following device: A piece of stiff platinum gauze about fifty mm. in diameter is bent into the form of a shallow dish, and to the edge is soldered a thick platinum wire which hooks over the edge of the beaker, suspending the gauze about forty mm. below. The saturated copper solution is poured on the drillings in the gauze (to remove air-bubbles) until it is covered, and the beaker allowed to stand until complete solution has occurred. This will require from one to four hours, depending on

the fineness of the drillings; if convenient, it may stand over night.

The carbon, nearly all of which in the case of the harder varieties of steels, remains in the gauze, is washed back into the beaker, and after settling a short time, is filtered in the usual manner.

Although a larger quantity of the copper solution must be used, and a longer time is required for dissolving in this way, yet the ease of filtration and washing is a sufficient compensation; especially in the analysis of steels of over 0.20 per cent. of carbon, when the residue retains the form of the original drillings, and may be washed entirely by decantation.

In the softer steels where the drillings are in the form of lumps, a little gas is evolved during solution, which, however, is nearly odorless.

#### COMBUSTION OF CARBON IN AIR.

The carbon separated from steels, I find may be burned completely in a current of air, dispensing with the use of oxygen which is frequently difficult to purchase of the desired purity. The combustion should proceed rather slowly, the roll of copper oxide in front of the boat being kept at a dull red heat throughout.

#### PRECIPITATED BINOXIDE OF MANGANESE.

When manganous nitrate in solution in strong nitric acid is heated with potassium chlorate, a precipitate of manganese binoxide forms, in which the manganese may be estimated gravimetrically, or calculated from the weight of the extra atom of oxygen found volumetrically. Many chemists aver that the latter proceeding always yields lower results than the former, presumably because an oxide lower than the binoxide is coprecipitated, *e. g.*,  $10 \text{ MnO}_2 + \text{MnO}$  (Stone, *Trans. A. I. M. E.*, 11, 327 and 12, 517); while others deny this, claiming, with good reason, that in such a strongly oxidizing solution, no such lower oxide could be formed (Mackintosh, *loc. cit.*, 12, 79 and Troilius, 12, 75).

An observation of a large number of determinations made on the same samples by both methods seems to prove that a greater or less discrepancy is always to be found; for example, on a

ferromanganese of eighty per cent., a difference of upwards of one per cent. is frequently obtained ; while in steel the results are practically identical.

It has occurred to me that the explanation of this fact was simply that more or less (according to the conditions of dilution, etc.) manganous nitrate was carried down mechanically enclosed in the precipitating binoxide, and from which, as in the analogous case of barium chloride occluded in barium sulphate, it cannot be removed by washing with nitric acid or water. It is found that when the solution of manganese contains ferric nitrate, a small quantity of iron is precipitated with the binoxide ; this may be ferric nitrate enclosed in the same manner, and where the amount of manganese or of iron in solution is relatively large, one would expect to find a greater quantity in the precipitate.

#### USE OF HYDROGEN PEROXIDE.

In the analysis of steel or iron, a dilute solution of this reagent may be used with advantage to dissolve the manganese binoxide precipitated by potassium chlorate, the excess being found by titration with 1-20 normal permanganate. For this purpose it has been employed for some years in this laboratory with good results, being used without filtration of the nitric acid from the manganese binoxide, as it is unaffected by dilute nitric acid and the slight excess of chlorine present. One molecule of manganese binoxide is reduced by one molecule of hydrogen peroxide ; and one molecule of permanganate of potassium by five molecules of the peroxide.

#### PHOSPHORUS IN PHOSPHOR-BRONZE.

When some samples of phosphor-bronze are dissolved in diluted nitric acid, the phosphorus is acted on in a similar manner to that in iron and steel, a portion of it passing into a combination with oxygen which does not combine with metastannic acid, nor is precipitated by molybdic acid. It is advisable, therefore, to complete the oxidation by evaporating the filtrate from the metastannic acid with chlorate of potassium, or otherwise, and then to test with molybdic solution. Occasionally



samples of phosphor-bronze yield as much as seven per cent. of the total phosphorus in the solution; others show only traces.

LABORATORY ILLINOIS STEEL CO.,  
SOUTH CHICAGO.

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### PATENTS OF INTEREST TO CHEMISTS.

EDITED BY A. H. WELLES.

*Nitric Acid.*—Oscar Guttmann makes nitric acid by forming gaseous nitric acid in a distilling chamber, conducting it in a tube to a condenser and introducing an air-blast into the tube to act upon the gaseous nitric acid before condensation (491,481).

*Starch.*—Julius Dubiel has a process for the manufacture of starch (493,689).

*Fertilizers.*—To make fertilizer from tank water, O. T. Joslin (489,090) evaporates the water to a thick sirup, adds a small per cent. of sulphuric acid and from five to twenty per cent. of magnesium sulphate, absorbs the supernatant liquid with some suitable substance and dries the mass at 300°–400° F. and grinds.

*Cattle Food.*—Arno Behr treats Indian corn in aqueous solution with sulphurous acid, separates the starch as usual, adds sulphuric acid to the steeping water, evaporates, and adds an absorbent to form a rich cattle food (491,234).

*Sugar.*—489,879 is granted Carl Steffen for a process for obtaining sugar.

*Milk and Butter.*—A milk coagulating product is patented by Clarence P. Eyre, but the description is exceedingly vague as to the nature of the ferment used (491,416). Pepsin, gum arabic, and alum are claimed by S. C. Wilson (489,775) as a compound for increasing the yield of butter from milk, and David W. Hudson *et al.* proposes (489,814) to manufacture a so-called butter containing pure butter, sweet milk, and oil of cocoanut.

*Brewing.*—A. Hummel has a new process for the manufacture of beer (492,292), C. Heintz, a method and apparatus for purifying and softening liquors (492,542), and R. Rahr a process for making caramel malt (491,813). Moses Wool is granted 493,460 for a process for making brandy-mash and composition for same, and electricity is used by John Becker for purifying and ageing liquors (493,809). 490,538 is a process for preparing raw grain proposed by H. T. Brown. 490,056, Otto Zwietusch, patentee, is a process for making beer, and Arnold Kreusler (489,018) also has a new method of obtaining the same beverage, and E. A. Spink ages liquors in an original way (489,337).

*Filtering Apparatus.*—Simeon L. West has an apparatus for purifying, sterilizing, and filtering drinking water or other potable liquids (491,828).

*Disinfectant.*—Should the cholera come this year, as is feared, Albert

E. Woolf's disinfectant and deodorizer (490,797) ought to be a valuable one, containing as it does "chlorine, chlorides, hypochlorites, free oxygen, and ozone." What more could one desire?

*Grease Extractor.*—Benedickt Ehman employs a mixture of gasolene, sulphuric ether, alcohol, spirits of ammonia, powdered borax, powdered carbonate of soda, and saltpeter, for removing grease (491,413).

*Paints, Cements, etc.*—Finely ground mica is used as the base, which combined with oil, a pigment, and a binder forms a paint compound introduced by W. B. Abert (491,003). Robert R. Graf uses tungstate of ammonium, hyposulphite of ammonium, sulphate of soda, caustic lime, chalk, alum, carbonate of soda, and oil for a fire-proof paint (494,508). Vinegar, lime-water, salt, alum, white vitriol, linseed or other drying oil, and petroleum is the combination Richard J. Doyle uses (490,547) for a non-inflammable paint, and the same combination with the addition of from twenty-five to eighty-five per cent. of aluminum silicate in the form of soft unctuous clay (490,548) is used for a non-inflammable cement. Aluminum dissolved in glacial phosphoric acid, mixed with zinc oxide, which has been first "heated to reduce to a gummy condition," forms a base for a dental cement, which Max Sichel covers by 492,056. A cement composed of pulverized spent lime, pulverized carbon, silica, iron oxide, alumina, lime, magnesia, slaked rock lime, and sand is the invention of Bernard Dreyfuss (491,280).

*Patent Plasters.*—Herman Endemann is the patentee of a composition for artificial stone (489,377). Magnesia, magnesium hydrate, basic oxalate of magnesium, and sand are named. Air-slaked lime, glue, or oil cake, and china clay, are the ingredients of a compound used by Enos A. Bronson for retarding the setting of plaster (493,613).

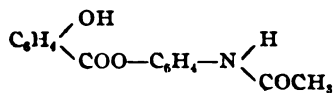
*Miscellaneous Compounds.*—Caroline S. Ely (493,693) names soda ash, ammonium sulphate, borax, oat and wheat flour, as a washing compound. R. B., J. L., and R. W. McEwen patent a process for forming paper board from old newspapers (492,927). Frank S. Culver patents a fire-proofing composition for wall covering containing asbestos fiber, clay, plaster of Paris, "Acme" cement, and a binding fiber (493,152) and James F. Thompson has a new burnishing composition (494,514). John F. Newell receives two patents on compositions for bearings: 494,156 mentions plumbago, fibrous substance, red lead, white lead, and a drying oil; and 494,433, plumbago, fibrous substance, an oxide, carbonate or basic carbonate of lead. James L. Covell describes his material for covering pipes as consisting of wheat flour, pulverized alum, arsenic, red lead, litharge, beef gall, and water (491,836). Richard V. Mattison has taken out three patents: one (492,092) is for a non-heating composition composed of calcium carbonate, magnesium carbonate, and asbestos; the second (492,093) is a boiler covering composition containing magnesium carbonate, plaster of Paris, asbestos, and wood pulp; and the third is similar (492,094) with the exception that calcium carbonate is

substituted for the plaster of Paris. Gustav Gumbel uses the waste liquors from the manufacture of sulphite cellulose, glue, and hydraulic lime, as a compound for "water-proofing oil receptacles" (491,284). A composition for leather for razor straps consisting of tallow, beeswax, molasses, and chimney ashes from burnt coal is the idea of Frank Minnis (490,030). Matthew H. Devey uses powdered slag, glass, and a binding medium for an insulating compound (490,641). George S. Lee (490,667) is granted the right to use "asphaltum, distilled coal-tar, residuum of petroleum, disintegrated paper, or wood pulp, and air-slaked lime" for the ingredients for a patent pavement. David A. Wray (491,395) uses tar or the residuum, or heavier products of oils, mixed with chloride of sulphur and chloride of iron, for a roofing and paving composition. Ludwig Haarmann secures a surface of asphaltic mastic by first coating with a solution of a bituminous substance, and applying mastic after evaporation of the solvent (492,197). A new compound of blown oils is described as "blown, non-drying glycol ether of an unsaturated fatty acid, combined with pyroxylin or nitro-cellulose," and Walter D. Field is the patentee (491,880). Plumbago, white lead litharge, and asbestos, and a binding or cementing substance as resin, or gum copal in linseed oil, is claimed by John T. Richards as a composition for journal bearings (492,750). Byron B. Goldsmith produces nitro-cellulose or celluloid surfaces by coating with pyroxylin varnish and varnishes containing resin (490,195). That indefatigable worker, Thos. A. Edison, has an improvement (490,954) in the manufacture of carbon filaments for electric lamps.

*Dyes and Dyeing.*—Charles Noroy (493,286) first dips goods to be dyed black into a bath of water, logwood, and a copper salt, then immerses in a fixing bath, composed of "neutralized nitrated starch," alum, metallic sulphates, potassium bichromate, and a small quantity of soda or ammonia. Leopold Le Blois has a method and apparatus for bleaching or dyeing textile materials (489,819). Bruno Beyer treats silk waste to the action of oil soap, cold water, and salt steam baths, dries, and then subjects to the action of potassium permanganate (489,919). Frank P. Pearson (491,951) and George Donald (491,961) patent processes for printing colors with aniline black, as well as Wm. Browning (491,673). Robert Gnehm and Jakob Schmid introduce a new brown dye (491,422), the sodium salt of an azo-derivative of meta-diazo-benzoic acid and Bismarck brown; Theodore Diehl derives a new blue-black azo dye (491,410), Jakob Schmid and Johannes Mohler, a new violet-blue induline dye, prepared by melting a mixture of para-phenylene-diamine, hydrochlorate of para-phenylene-diamine, and alpha nitro-naphthylamine at 160° to 190°, dissolving the melt in hydrochloric acid and precipitating with common salt (491,378). Bruno R. Seifert obtains a dye from alpha oxyvitic acid (493,143); Herman Boedeker, a pink dye, the alkali salt of a sulphonic acid, derived from fluorescein chloride and mesidine

(493,241). Jakob Schmid has a blackish blue azo-dye (493,563) and a gray-black tetrazo-dye (493,564), and Jakob Schmid and Robert Gnehm patent a red azo-dye (493,583). Mr. Schmid and R. Pagapini prepare mono-sulpho-dioxynaphthoic acid by heating the sodium salt of di-sulpho-beta-oxy-naphthoic acid with caustic alkalies at 200° to 260°, and precipitating the dissolved melt with hydrochloric or sulphuric acids (493,562). 489,623 is granted Fritz Bender on a "yellow-red" dye, by oxidizing the bluish-red dye-stuffs derived from dialkylmeta-amido phenols. Albert Herrmann (490,408) derives a new color from tetralkyl-diamido-triphenyl carbinols, a copper-red powder with metallic luster, "soluble in water, insoluble in alcohol and benzine, dyeing wool and silk in acid bath very uniform blue shades." Professor Peter T. Austen incorporates an alkaline nitrate with logwood extract, producing thereby a friable solid, soluble in cold, and very soluble in hot water (491,972). He uses a similar method in preparing a solid coloring matter from fustic (492,368), and to cure logwood chips, adds a solution of a nitrite (494,237).

*Organic Compounds.*—Joseph Berlinerblau (489,728) prepares para-phenetol carbamide by treating para-phenetidin or para-anisidin with phosgene, adding ammonia to the products, and crystallizing out the resulting compound. R. P. Pictet (489,552) purifies commercial chloroform by cooling to 80°–82°, filtering the cold mass, crystallizing the chloroform, separating the non-crystallizable part, and finally distilling the chloroform at a very low temperature, and collecting the middle products. An antiseptic and antineuralgic compound, derived from salicylic acid, is patented by Herman Jaussen (492,868). It has the formula



### NEW BOOKS.

LECTURE NOTES ON THEORETICAL CHEMISTRY. BY FERDINAND G. WIECHMANN, PH.D., INSTRUCTOR IN CHEMICAL PHYSICS AND CHEMICAL PHILOSOPHY, SCHOOL OF MINES, COLUMBIA COLLEGE. New York: John Wiley & Sons. 12mo cloth. Price, \$2.50.

A handy little volume of 225 pages, nicely put up both in type and paper, and intended to aid those entering upon a study of theoretical chemistry, more particularly those attending lectures on this topic.

The book differs in many respect from others dealing with the same subject. It does not pretend to philosophically survey and critically sift the existing theories in chemistry; it does

not address chemists who have been actively working for years, and who, perhaps, have arrived at distinct ideas of their own about the value of this or that theory in regard to the observed regularities and constants in chemical action. It addresses college students, accompanying them during the very time of their laboratory work. This is evident from the fact that the first eight chapters are almost exclusively explanatory of methods employed in the laboratory for making certain determinations such as specific gravity of solids, liquids, and gases, or explanatory of terms used in chemistry. The American spelling and pronunciation of chemical terms as adopted by the American Association for the Advancement of Science in 1891 has been fully reproduced at the end of the third chapter, which begins with the oldest chemical terms and gives the notation of the alchemists.

Chapters treating on valency, on the writing of chemical equations, and a very perfect description of chemical calculations, illustrated by numerous examples, follow.

It seems to us desirable that the sixth chapter, which devotes but half a page to "isomerism" and three pages and a half to "stereochemistry," should be elaborated more fully in the next edition.

The ninth chapter treats of the periodic law, and this as well as the following chapters down to the end, formed by chapter 14 on electrochemistry, include in a very small space a great deal of matter important to the understanding of the outlines of theoretical chemistry.

The methods of measuring osmotic pressure are indicated, but not as perfectly treated as the methods treated in the earlier chapters dealing with specific gravity and vapor density, evidently for the reason that students are not called upon to practically perform these determinations, which lie beyond the range of practical college laboratory work.

The chapters on thermochemistry and electrochemistry are concise and abound in practical data.

As a sign of honest work and at the same time a welcome help to the student we find at the end of the book ten pages of bibliography. An alphabetically arranged index of subjects as well as of names cited finishes the volume.

F.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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[CONTRIBUTIONS FROM CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE.—No. 4.]

### LAMP FOR CONSTANT MONOCHROMATIC FLAME.<sup>1</sup>

BY H. W. WILEY.

Received May 3, 1893.

IN optical experiments requiring a constant monochromatic flame there is great difficulty in securing an intensity of illumination which remains constant for an indefinite time. The ordinary lamps, for instance, producing a sodium flame, are fed by introducing, from time to time, fragments of fused salt into a platinum mesh spoon which touches the edge of the flame. The intensity of the illumination at the time of adding a fresh portion of the fused salt is great, but after a few minutes there is a sensible difference. For this reason, polarimetric observations are rendered somewhat difficult, inasmuch as the instrument which is set at zero with one intensity of illumination would vary somewhat from that with a different illumination. Probably this would not be the case if absolutely pure chemicals could be used. The only difference then would be in the intensity of the light. In point of fact, however, a difference in the color of the light is often disclosed with the lamps of ordinary construction, so that an instrument which is set at zero at the moment a fresh piece of fused salt is placed in the flame would not show the same zero after the salt had been ignited for some time.

To avoid such difficulties as these and secure a constant,

<sup>1</sup> Presented to Washington Chemical Society, April 13, 1893.

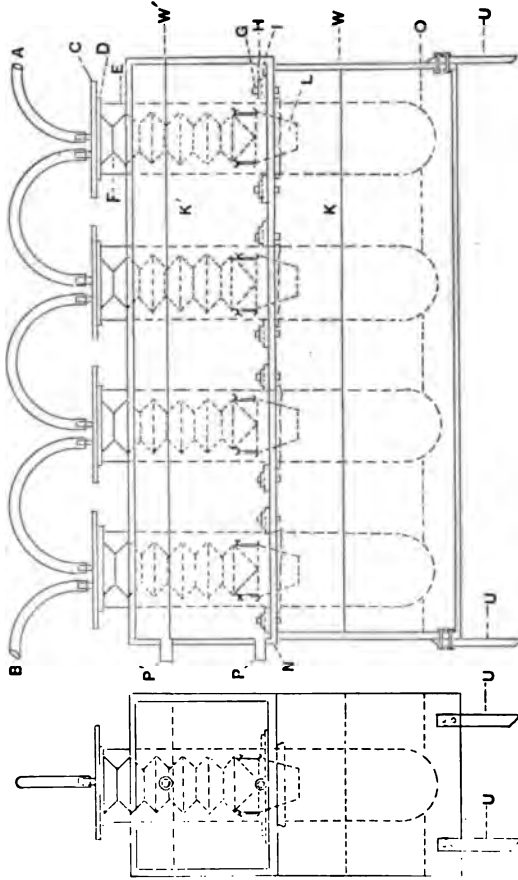
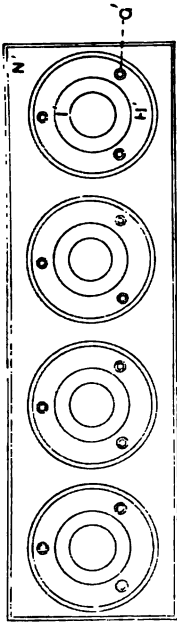
which the tubes pass water-tight. The plan of the bottom is shown in figure H' N' G'. The rubber diaphragms are held by two brass rings fastened together by small bolts. One of these rings is placed below the perforated bottom and one above. The perforation of the rubber diaphragms is shown at I'. An end view of the box is also shown at the left of the illustration.

This box has two exits, P and P', so that water can be allowed to flow in a thin film over the bottom and escape at the exit P, or if the exit P be closed the water can be made to rise to the level of P' as shown by the line W'. The outside of the test tubes can in this way be surrounded with water, or if a lower temperature be required fragments of ice can be dropped in. The object of this is to condense the vapors of the solvent which may strike against the sides of the tube and thus tend to rise to the top and escape at the intersection of the metal plate and the ground glass rim of the tube.

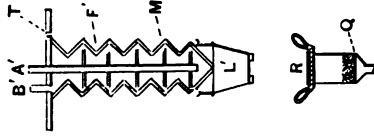
The baths are made of convenient size to hold four of these tubes and the condensers can all be cooled with a single stream of water entering at A and after passing through the four condensers escaping at B. A section of the condenser is shown at the right of the illustration. The water enters through A' and passing upward round the disks M is thrown to the outside of the condenser and escapes at B'. The vent at T is left open until the vapor of the solvent has filled the interior of the apparatus, when it is closed.

The material to be extracted may be held in the perforated crucible L' or an ordinary glass extraction tube, R, Q, with a perforated platinum disk fused into the glass at Q, and carrying an asbestos felt, can be employed. The upper part of the glass extraction tube has a little flange on it to support a looped wire, by means of which it can be hung to the hooks on the condenser in the same manner that the crucible is supported. The advantage of using glass is that the operator can see every thing which is going on in the extracting tube.

When the apparatus is to be used with ether the box K' should be lifted up from K and the extraction tubes thrust farther through the diaphragm, until at least one of the corrugations of the condenser passes below the diaphragm. Otherwise



IMPROVED EXTRACTION APPARATUS.





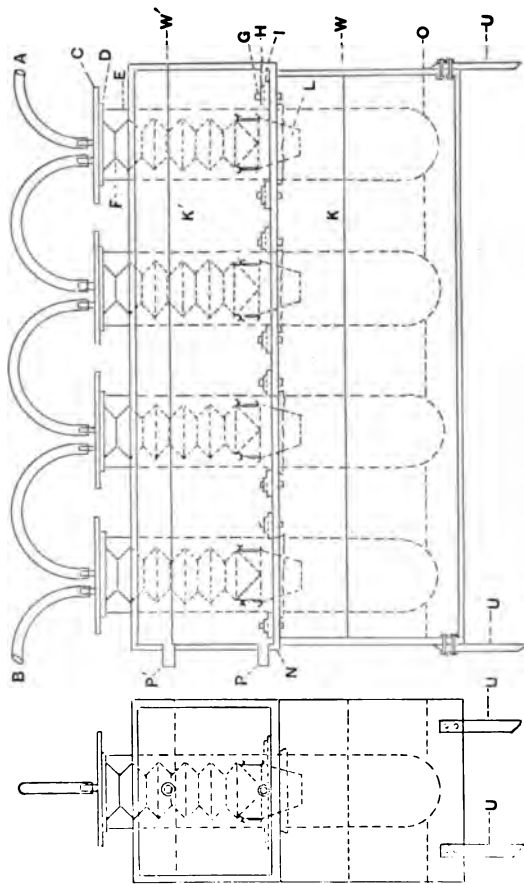
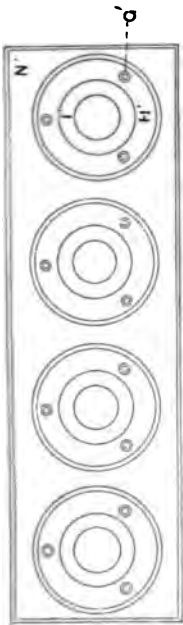
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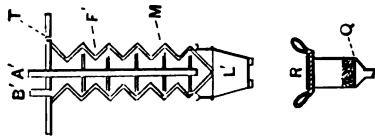
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IMPROVED EXTRACTION APPARATUS.





the ether will be largely condensed on the sides of the glass test tubes and will run back down the sides instead of being collected on the condenser and dropped into the extraction tube. The box K', for this purpose, can be held on any convenient support. When ether is used the vent P is closed and the one at P' left open and a stream of water is made to flow into the box at the end opposite P' so that the water in K' is continually changing. This avoids any objectionable loss of ether by its escaping at the top of the apparatus.

When eighty per cent. alcohol is used for the extraction the vent at P is to be left open and sufficient water allowed to run in at the end opposite P to keep the bottom of the box K' cool. The vapor rising from the box K is condensed by this cooled surface so that it drops directly back into K. When alcohol is used the box K' should rest directly upon K.

With eighty per cent. alcohol the boiling point of water is not quite sufficient to secure a rapid evaporation of the solvent. A mixture composed of two parts of glycerol and one part of water will be found most convenient for this purpose. Inasmuch as many of the substances extracted by alcohol give up a large quantity of matter to the solvent the boiling point is therefore considerably raised and the glycerol bath is necessary in this case to secure a sufficiently rapid evaporation. To avoid any danger of bumping with such alcoholic solutions, it is convenient to add a few fragments of platinum foil.

The residues in the test tubes can be dried and weighed in the tubes or the amount of the extracted matter can be determined by weighing the crucibles or glass tubes containing the matter to be extracted. The latter method is preferable, with perfectly dry substances inasmuch as it is possible especially with ether that some bodies may be extracted from the material which are subsequently volatilized during the drying of the extract. Whenever it is desired to weigh the extract, especially the ether extract, it may be received in a small cylindrical glass vessel with flat bottom, four to six cm high and of a diameter just permitting its introduction into the extraction tube. About ten cc. of mercury are first poured into the extraction tube on which this vessel rests. The necessity of weighing the heavy

test tube is thus avoided and the extract is more easily dried in the small vessel.

This construction of the apparatus is compact, occupying but a small space ; is easily manipulated, requiring but little attention, and is economical in respect of the use of gas, a single lamp being sufficient to operate a bath containing four tubes. It has the additional advantage that all parts are open to inspection so that the progress of the extraction can be watched at all times if necessary. It also has the advantage that both the extract and the residue can be weighed and thus a check on the results be obtained. The volatilization of the solvent should be so regulated as not to accumulate any liquid in the extracting tube.

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## ABSOLUTE ALCOHOL.

### SECOND PAPER.

BY EDWARD R. SQUIBB, M. D., OF BROOKLYN, N. Y.

Read before the New York Section, June 2, 1893.

A VERY considerable experience in the manufacture of so-called "absolute alcohol" for the market up to 1884 convinced the writer that really anhydrous alcohol had not yet been obtained.

During the latter part of 1883 and the early part of 1884 the subject was investigated with care, and the results were published by the writer in the *Ephemeris* for May, 1884, 2, 522. This paper opens with the following paragraphs, which are as true to-day as they were ten years ago :

"It appears to be very certain that no alcohol has as yet been rendered entirely anhydrous, and therefore the term 'absolute,' as applied to any yet made, is not strictly correct. For all practical purposes, however, it is a very convenient term by which to designate a rather indefinite substance, but one now applied to a great many important uses, and therefore itself growing in importance.

"It is not difficult to get alcohol practically free from all impurities, including water as one, but to free it from the last one-thousandth part of water is very difficult indeed—so difficult, that traces of this ultimate fraction of water have, so far, always been retained. Hence in considering it as absolute alcohol, it can only be regarded as being freer from all other impurities than from water, and as being more or less free from

water. No alcohol should be called absolute, however, that contains less than 99.4 per cent. by the best determinations. When carefully freed from all impurities except water, specific gravity becomes a very accurate indication of strength, and it has always been relied upon as the decisive test of strength. For many years each careful observer reduced the specific gravity little by little to those specific gravities upon which the tables of the present day are based, by using new appliances which the progress of knowledge supplied, and the object of this note is to show that improvement in these appliances is not yet at an end."

The paper then goes on to show that by slow, cold percolation through quick-lime and simple distillation, alcohol in large quantities had been obtained that was of lower specific gravity than the lowest given by the best of the authorities on the subject. Over thirty determinations were found, and hardly any two of these were in fair accord. Some of the best and most generally quoted of these authorities are examined and discussed with the conclusion that it is particularly unfortunate that the three most generally accepted authorities should, by the construction of their elaborate tables upon erroneous bases, have misled the world for so many years upon this enormous alcohol interest.

Then, commencing with an alcohol that was already below all the authorities found, and yet known to contain traces of water, the attempt was made to reach a still lower degree of hydration. The means adopted, and the checks upon the work, and the results are carefully described in detail with the hope and expectation that more capable hands would go over the work to correct or confirm it, since it was much too important to be accepted without confirmation by other investigators. Nearly nine years have now passed since the publication of this paper, and yet notwithstanding the importance of the subject, no further investigations have been noticed.

The specific gravities previously reached were, at  $\frac{15.6^\circ}{15.6^\circ}$  C., 0.7938<sub>11</sub> (Drinkwater);<sup>1</sup>  $\frac{15.6^\circ}{15.6^\circ}$  C., 0.7938 (Fownes);<sup>2</sup>  $\frac{15.6^\circ}{15.6^\circ}$  C., 0.7939 (Tralles);<sup>3</sup>  $\frac{15.6^\circ}{15.6^\circ}$  C., 0.79367 (Mendelejeff).<sup>4</sup> This last specific gravity when brought to the terms of the others, namely  $\frac{15.6^\circ}{15.6^\circ}$  C., is 0.79391.

<sup>1</sup> Quoted from *Memoirs of the Chemical Society*, 3, 450.

<sup>2</sup> Quoted from *Fownes' Manual of Chemistry*, third edition, 591.

<sup>3</sup> Quoted from *Wall's Dictionary of Chemistry*, 1888, 1, 95.

<sup>4</sup> Quoted from Roscoe and Schorlemmer, *Treatise on Chemistry*, 3, Part I, 299.

The specific gravity reached at that investigation was, at  $\frac{40}{40}$  C., 0.802566; at  $\frac{15}{40}$  C., 0.793260; at  $\frac{15.6}{40}$  C., 0.79279; at  $\frac{25}{40}$  C., 0.78496; at  $\frac{15.6}{15.6}$  C., 0.79350; at  $\frac{25}{15.6}$  C., 0.78573. Thus the reduction of specific gravity effected by the work of that paper was from about 0.79380 to 0.79350 at the temperature of 15.6 C. (60° F.) compared with water at the same temperature of 15.6 (60° F.), or 0.00030, which in strength is equivalent to nearly one-tenth of one per cent.—0.000338 being the difference in specific gravity for 0.10 per cent.

Judging from the circumstances attending the percolations and distillations and from the want of constancy in the boiling point as shown by slight differences in specific gravity of different fractions of distillate, the writer was convinced that this alcohol was not quite anhydrous, and supposed that by modification of process and by better management a specific gravity of about 0.79340 should be attained. The further experience of the past nine years has rather tended to confirm that judgment, and therefore it was concluded to return to the subject at this time, and to review the former work with different methods and some modifications of process, and some improvements in apparatus suggested by longer experience.

#### APPARATUS OF PRECISION FOR THE SPECIFIC GRAVITY OF LIQUIDS.

As specific gravity is the sole indication of strength to be relied on, and as alcohol changes very much in volume by changes in temperature, accurate and highly sensitive apparatus was of the first importance in the determination, and it was thought that improvements could be made in the apparatus formerly used.

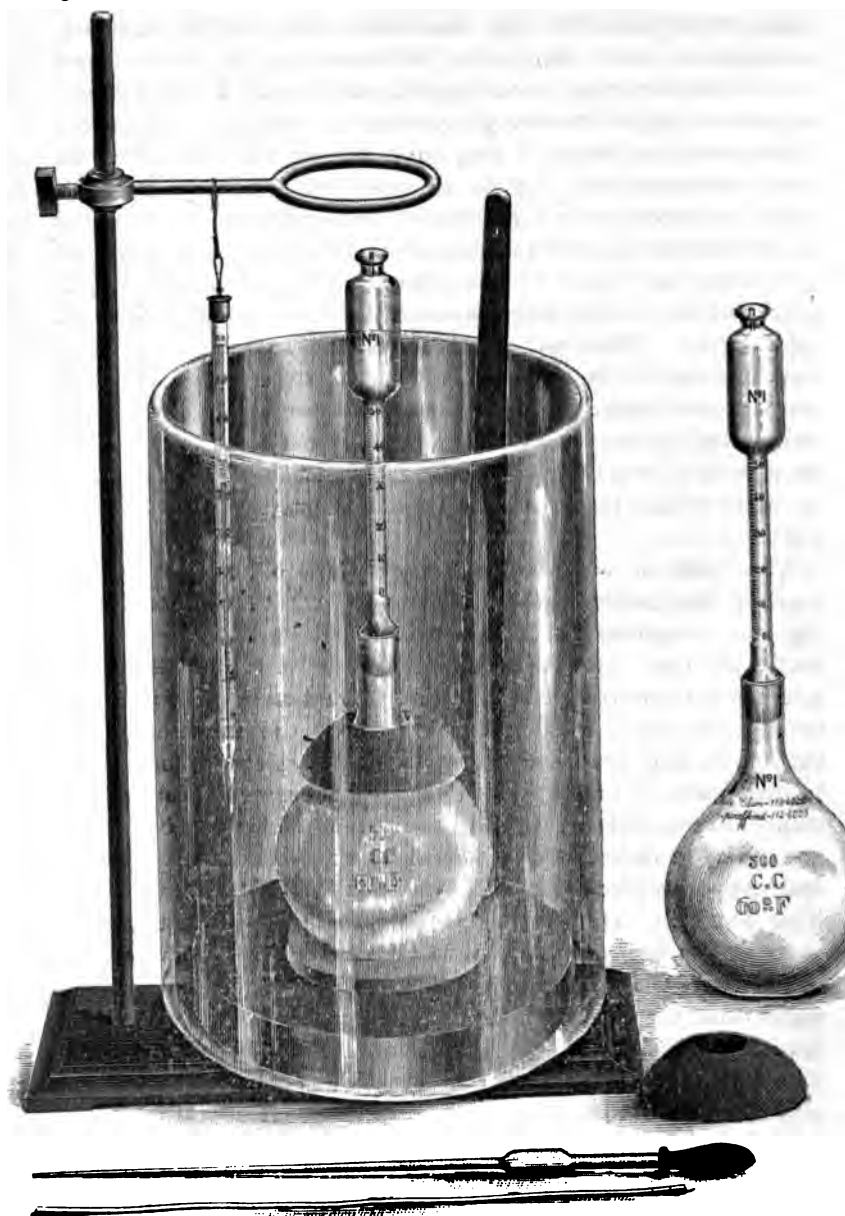
A standard thermometer was used, made by Hicks of London from Powell glass, standardized and graduated at Kew in 1884, about eight years after it was made. This instrument had its present error determined by comparison with the international standards at the U. S. Bureau of Weights and Measures in Washington through the kindness of the superintendent, Prof. T. C. Mendenhall, and its indications of temperature were read to 0.1° C.

Several very accurate specific gravity bottles of 100 and 500

grams were used, but the one relied upon for the final determinations, and shown in the accompanying cut, is supposed to be an improvement upon any hitherto described. The device of constructing a specific gravity bottle upon the design of a thermometer by having a long tube stopper was carried out for the writer many years ago by an expert Paris glass blower, but it had no provision for expansion of the liquids without loss, and was too tall for any ordinary balance. The design was improved and carried out better by the writer in 1884 (see *Ephemeris*, 2, 529), and was still further improved in 1889 (see *Ephemeris*, 3, 1162-1166). There was, however, still a recognized defect, in want of room for the expansion of liquids in warming up to room temperatures before weighing, and in so limiting loss by evaporation during expansion and weighing, that a practically constant weight could be attained. This last improvement seems to fairly satisfy these conditions, and in practice answers very well.

The bottle is an ordinary 500 cc. flask old enough to have reached its maximum contraction, and so large that errors of reading and weighing are well within the design of reaching the sixth decimal place with tolerable accuracy. A flask was selected with narrow neck, and the graduation mark low in the neck. The neck was cut off just above the mark and was thickened and shaped for stoppering. A piece of barometer tubing fifteen to twenty cm. in length was expanded into a long stopper at one end and carefully ground into the flask neck. Then 500 grams of recently boiled distilled water was put into the flask and stopper and the whole cooled in an iced bath to  $4^{\circ}\text{C}$ . ( $39.2^{\circ}\text{F}$ .). The water in the tube stopper should then be near the lower end, but if not, the end is ground off until the meniscus for  $4^{\circ}\text{C}$ . is just above the ground part of the stopper. The 500 grams of water and the  $4^{\circ}\text{C}$ . temperature being then again accurately adjusted, a mark was made at the lower limb of the meniscus. The bath was then warmed up to  $25^{\circ}\text{C}$ . ( $77^{\circ}\text{F}$ .) and when the water had ceased to rise in the tube after the temperature of the bath had been held constant for half an hour, another mark was made, the tube being of such a caliber that the two marks should be about ten cm. (four in.) apart. Any excess in the length of





APPARATUS FOR SPECIFIC GRAVITIES OF LIQUIDS.

the tube above the upper mark was then cut off, and a liberal section of a very much larger tube was put on. This larger portion was about 2.4 cm. (one in.) in diameter, and about seven cm. (2.75 in.) long, drawn into a narrow neck at the top, and the neck fitted with a flat ground glass stopper which had a capillary passage through its center. The tube portion of the stopper was then graduated in fifty equal subdivisions, the scale beginning with 0 at the 4° C. point, and extending to fifty at the 25° C. point. These subdivisions are easily and accurately read to half divisions so that the scale is read to hundredths. Then upon accurate readjustment it was found that the reading with recently boiled distilled water was one—that is  $\frac{1}{100}$  of the scale from 4° C. to 25° C. The reading at 10° C. was six, or  $\frac{6}{100}$  of the scale. At 15° C. the reading was twenty-five. At 15.6° C. (60° F.) it was twenty-eight. At 20° C. it was fifty-seven, and at 25° C. (77° F.) it was 101. These readings illustrate in a very interesting way the rapidly increasing ratio of expansion for water. Without correction for expansion of the flask the increase in volume for 25° C. (4° to 25°) is just 100 divisions of scale, giving a mean value of  $4.76 \pm$  divisions to each 1° C. But the expansion for the first six degrees (4° to 10° C.) is only six divisions of scale, or one division to each 1° C. while the expansion for the last five degrees (20° to 25° C.) is forty-four divisions, or 8.8 divisions to each 1° C. This scale adapts the flask to taking specific gravities at all the ordinary standards of temperature, and adapts it to correction by readjustment at any time in case of contraction of the glass by age. It also enables the observer to watch the changes in height of the column of liquid and to know accurately when it ceases to rise or fall. When accurately adjusted the weights were taken on a fine balance to 0.0001 gram when chemically clean, and also when the stopper was lightly lubricated with soft paraffine,—these tares being etched upon the bottle, and all the readings of the standard water being entered in the laboratory note book.

#### BOTTLE IN USE.

The bottle, properly filled, and loaded with a leaden collar to steady it, was always used in a glass water-bath, the water of the bath being kept above the level of the reading lines, and

these read through the glass and water. The thermometer was suspended in the bath with the bulb opposite to the upper part of the bottle, and was also read through the glass and water; and a wooden stirrer was used to keep the water uniform throughout. When the temperature of the bath had been held steady to the required temperature for ten minutes after the column in the tube had ceased to rise or fall, the adjustment to the required graduation mark was made by passing the long capillary pipette and the very narrow strip of blotting card paper, shown in the cut, down through the tubulure in the stopper. In order to know how nearly the temperature of the liquid in the bottle agreed with that of the water of the bath, a pair of compared thermometers were used, and it was found that with either water or alcohol in the bottle, the temperatures were in accord to about  $0.05^{\circ}\text{C}$ . after all perceptible change in the column had ceased, and the bath had been held constant for five minutes; and upon this experience ten minutes was adopted as the uniform time of waiting before the final adjustment. Then it was found that no constant weight of bottle and contents could be obtained so long as these differed more than one or two degrees from the room temperature of scale-case and weights, and therefore a second bath was used after adjustment to bring them accurately to room temperature, and then they were allowed to stand on the balance with the case closed until they reached a fairly constant weight. As all this management required time, it became necessary to know whether there was any material loss in weight between the time of adjustment and the final weighing, and on trial it was found that with water the bottle and contents, either in the bath or out, did not alter perceptibly in weight within forty-eight hours, and with the alcohol under the same conditions, the loss in a warm room was not greater than 0.04 gram in forty-eight hours, or less than one milligram per hour. This loss was therefore neglected as being well within the sphere of unavoidable errors.

The weighing was done upon a large balance sensitive to 0.002 gram, and this was readjusted for each accepted critical weighing. The weights used were of brass, of a specific gravity of about 8.383, with platinum fractions of a gram. They were not stand-

ardized, but as they agreed among themselves, and as all the weighings were made with the one set, this gave no source of error. The critical weighings were made with the barometer not far from 760 mm. (thirty inches), and no correction for barometer was attempted. All weighings were made against water at the same temperature taken as unity, and therefore corrections for expansion of glass were avoided. Neither were any corrections attempted for the use of brass weights, because such corrections take the results out of the range of ordinary daily practice and tend to confusion rather than to practical utility. As the weighing was done to 0.002 gram in a 500-gram bottle the results are stated to the sixth decimal place, and although the sixth decimal cannot be trustworthy, even to twice the indicated value, it is still believed to be of more value than if expressed in the nearest unit of the fifth place. In view of the rapidly increasing importance of specific gravities of liquids, it is very desirable to give a more definite value to this sixth decimal place. The writer has 100-gram specific gravity bottles of the same construction which can be easily weighed on a fine balance to 0.0001 gram, but as yet the measuring or volume adjustment cannot be brought up to this high degree of precision.

#### LIME PERCOLATOR.

It was confidently expected that a more perfect dehydration might be obtained by often repeated percolation through lime than by the former process of prolonged shaking with lime, provided the percolation could be done without air contact, as was not done in the processes of the former paper.

A very large calcium chloride jar, holding almost a kilogram of lime, with large chamber below, was nearly filled with strata of granulated quick-lime alternately fine and coarse, the whole supported at the contraction below on a layer of glass wool. At the top a rubber stopper with two perforations was used, supplied with two glass tubes bent twice at right angles, the short leg projecting just through the stopper, while the long leg extended downward outside the jar. The tubulure of the chamber below was fitted with a rubber stopper of one perforation supplied with a glass tube, bent downward within so as to draw all the liquid

out, and bent upward without to receive rubber tubing. The object was to deliver the alcohol on top of the lime, draw it through the lime by means of the Sprengel water-pump, and then draw it out of the chamber below the lime to be again passed on top, and again through the lime, and this without contact with any air that had not been thoroughly dried. Near the lime percolator on each side was placed a bottle of two liters' capacity, each fitted with rubber stoppers supplied with a long and a short tube, the short tube passing just through the stopper, and the long one going to the bottom and so bent that its end reached the very lowest point in the bottle. A little farther off from the percolator on one hand was a large apparatus for drying the inspired air, and on the other hand the Sprengel water-pump. In the drying apparatus the air entered through a tube filled with caustic baryta, then bubbled through concentrated sulphuric acid and then ascended through a large jar of calcium chloride to the outlet. By means of rubber tubing and glass T and Y tubes these various parts were so connected that by means of screw pinch-cocks some passages could be stopped and others opened to the effect that the alcohol was easily and conveniently drawn from one bottle upon and through the lime into the other bottle, well dried air taking its place, until the bottle was empty and its fellow on the other side full. Then the closed pinch-cocks were opened, and the open ones closed and the alcohol was drawn back through the percolator to the other bottle, and so on. With a partial vacuum of only about 100 mm. (four inches) about four of these percolations were made in a day, and generally the alcohol was passed through about twenty-five times before being distilled.

#### APPARATUS FOR THE DISTILLATIONS.

The distillations were all made in one arrangement of apparatus. A round bottomed flask of about two liters' distilling capacity was held on a round bottomed water bath over a gas flame. The flask was fitted with a good cork that had been well dried by immersion in hot paraffine. This cork was perforated for a small tube through which to aspirate dry air, or the charges of alcohol, and also for the large end tube of a Hempel tube

about thirty-five cm. (13.7 inches) in total height, the passage of this tube through the cork being made air-tight by means of paraffine. The Hempel tube was then three-fourths filled with small glass marbles, and from the end of this tube, in the flask, a thermometer was hung. In the bottom of the flask, to prevent explosive boiling, was put a liberal supply of recently ignited fragments of clay, tobacco pipes, and platinum scraps. From the top of the Hempel tube a vapor tube of liberal size, bent twice at right angles, led to the condenser. The condensing tube was of thin glass, about seventy cm. (27.8 inches) long, turned up at one end to receive the vapor tube from the Hempel and bifurcated at the other end, each branch having a well ground glass stop-cock, well lubricated with soft paraffine—the ends of the branches beyond the stop-cocks being contracted and turned down. About fifty cm. (19.75 inches) of this tube passed water-tight through a tinned iron trough capable of holding a good supply of broken ice and water. The two terminal ends of the condenser were connected by rubber tubing with short straight pieces of glass tubing which passed through one hole of two two-hole rubber stoppers. The second hole of each stopper was fitted with a bent glass tube, and these were connected by rubber tubing with the aspiration tube of a competent Sprengel water-pump. The two rubber stoppers, through which the small glass tubes passed, fitted all the specific gravity bottles, and the arrangement admitted of distilling into one or the other bottle at will, and of changing bottles without the contact of much air, without interruption and without breaking the vacuum. The distillate was usually divided into seven fractions for each distillation. The first two in 100-gram specific gravity bottles, the third in the 500-gram specific gravity bottles, the fourth, sixth and seventh in 100-gram bottles, and the fifth in a 500-gram bottle.

In making the distillations the boiling was commenced under a partial vacuum of about 300 mm. (twelve inches), and without condensation in order that the pump might draw off all dissolved air and gases, and any liquids of low boiling point. Under this diminished pressure the boiling always began at about 50° C. (122° F.), and the temperature rose steadily to

about 67° C. (152.6° F.) before any considerable vapors went beyond the Hempel tube. Then the ice and water were put in the condenser trough, and the first 100-gram specific gravity bottle was filled under this partial vacuum. Then the vacuum was allowed to run down to about twenty-five mm. (one inch) and the remainder of the distillation was conducted under that slight minus pressure.

#### THE ORIGINAL ALCOHOL.

The following trials were all made with an alcohol that was always at hand in great abundance. It was believed to be quite free from all impurities excepting water and to contain only about 0.1 per cent. of water. The specific gravities taken with much care were as follows: At  $\frac{4}{4}$ ° C., 0.802818; at  $\frac{10}{10}$ ° C., 0.798018; at  $\frac{15}{15}$ ° C., 0.794258;  $\frac{15.6}{15.6}$ ° C., 0.793824; at  $\frac{20}{20}$ ° C., 0.790714; at  $\frac{25}{25}$ ° C., 0.787332. Provided the specific gravities given by Drinkwater, Fownes, Tralles and Mendeleeff were taken with as much accuracy as these now given here, this is the alcohol that, up to the date of these investigations, has been considered to be anhydrous, and it is the basis of all the best tables.

#### VALUE OF SPECIFIC GRAVITY IN PERCENTAGE.

Early in the investigation at this time, it became desirable to know with more accuracy than heretofore, the percentage value of specific gravities where there is so very little water present. To determine this point a portion of the original alcohol above described was used, and 1345.174 grams was carefully weighed off. To this portion 2.696 grams of distilled water was added giving a dilution of almost exactly 0.2 per cent. and the mixture was allowed to stand twenty-four hours, when the specific gravities were taken.

Specific gravity	At $\frac{4}{4}$ ° C.	At $\frac{10}{10}$ ° C.	At $\frac{15}{15}$ ° C.	At $\frac{15.6}{15.6}$ ° C.	At $\frac{20}{20}$ ° C.	At $\frac{25}{25}$ ° C.
Original alcohol	0.802818	0.798018	0.794258	0.793824	0.790714	0.787332
0.2 per cent. dilution	0.803434	0.798662	0.794932	0.794500	0.791362	0.787938
Difference for 0.2 per cent.	0.000616	0.000644	0.000674	0.000676	0.000648	0.000606
" " 0.1 " "	0.000308	0.000322	0.000337	0.000338	0.000324	0.000303

If these differences were interpolated and plotted they would give a form of curve for alcohol not hitherto known to this writer.

Next this portion of diluted alcohol was passed through the

lime percolator twenty-five times in six days to ascertain what proportion of this water might be abstracted by this treatment, and how near to a constant specific gravity or boiling point such alcohol would be. It had been recognized in the former investigations that a thermometer in the boiling alcohol was not an accurate indicator of the boiling point. In a clean glass flask the boiling was so nearly explosive that differences of a degree were often noticed within a very few seconds. Even with fragments of clay tobacco pipes and platinum scraps in the vessel the thermometer would rise and fall enough from time to time to preclude accurate observation of the constancy of the boiling point. The specific gravities of the fractions of distillate were, however, much better indications of the boiling point, since if these were constant, the boiling point would necessarily be also constant, and until these fractions were constant in specific gravity they could not be uniform in boiling point, and as long as they were not constant they could not consist of alcohol alone. That is, any mixture of two liquids as different in boiling points as alcohol and water could not distill at a constant boiling point, nor yield a distillate of constant specific gravity; and now it is known that a tenth of one per cent. of water in alcohol gives a very decided difference in specific gravity. The specific gravities given by the seven fractions of distillate from the portion of diluted alcohol that had been passed twenty-five times through the lime percolator were as follows, in the order in which they were received, all taken at  $\frac{15.00}{15.00}$  C.: First, 0.79414; second, 0.79403; third, 0.79402; fourth, 0.79400; fifth, 0.79392; sixth, 0.79400; seventh, 0.79404. Then all the fractions were put together and the specific gravity of the mixture was 0.793954.

These results are accepted as proving conclusively that no part of the distillate was anhydrous alcohol, and that about 0.16 per cent. of the water added was taken out by the lime, leaving about 0.04 per cent. of the water put in that was not taken out by the lime.

#### DEHYDRATION BY METALLIC SODIUM.

Many times in the literature of late years metallic sodium has been recommended for the detection of water in alcohol, and for depriving alcohol of the last traces of water. But such recom-



mendations were not easily understood in view of the fact that at ordinary temperatures sodium decomposes alcohol rather rapidly. It might, however, also abstract water. Then, too, the well-known influence of cold in modifying chemical action might be available, so it was concluded to try the effects of sodium at low temperatures. About two liters of the alcohol was well cooled in a bath of snow and salt to about  $17^{\circ}\text{C}$ . ( $1.4^{\circ}\text{F}$ .) and was held at that temperature or lower for about forty-eight hours. Throughout the day time of this period small pieces of sodium, two or three grams at a time, were dropped into the alcohol with the least practicable admission of air, and this was repeated five or six times a day, so that an aggregate of about forty grams of sodium was used. The sodium, instead of floating, went at once to the bottom, and the reaction was very moderate. This alcohol was then carefully distilled off from the sodium ethylate, the distillate being received in fractions, which varied considerably in specific gravity. The lowest fraction was, however, at  $\frac{15.60}{15.60}\text{C}$ ., 0.793713, and the average of the fractions was not below the 0.793824 of the original alcohol. This negative result is given because it may possibly save others from going over this ground.

*Experiment 1.*—A portion of good quick-lime was slaked with just enough water to make a fine dry powder. This was put into the center portion of a piece of three-inch wrought iron pipe, the two end portions being filled with quick-lime. Caps being screwed loosely on the ends the pipe was subjected to a dull red heat during four hours, and then cooled over night. About 500 grams of this lime was put into a bottle of 4.25 liters' capacity, and, 2.5 liters of the original alcohol having been poured upon it, the bottle was shaken half an hour at a time, in a mechanical shaker, during an aggregate of sixty hours in five weeks. The alcohol was then filtered off from all traces of lime, with as little air contact as practicable, and was aspirated into the distilling flask and distilled. The specific gravities of the seven fractions taken at  $\frac{15.60}{15.60}\text{C}$  were: First, 0.793851; second, 0.793839; third, 0.793680; fourth, 0.793701; fifth, 0.793679; sixth, 0.793400; seventh, 0.793701; an eighth fraction was 0.793620.

The sixth fraction of this series was rejected as being too low, and quite out of accord with the other elements of the series, but all the other weighings were trustworthy.

*Experiment 2.*—The mixed fractions from experiment 1 were passed through the lime percolator about ten times, and then again distilled, when the fractions gave the following specific gravities at  $\frac{15.60}{15.65}$  C.: First, 0.793960; second, 0.793801; third, 0.793582; fourth, 0.793639; fifth, 0.793606; sixth, 0.793576; seventh, 0.793549; second weighing of the seventh fraction gave 0.793499. At the first weighing it had not reached a constant weight, while at the second weighing, thirty minutes later, there may have been a very slight loss.

*Experiment 3.*—A fresh portion of the original alcohol was passed twenty-five times through the lime percolator, and distilled with the following results: First, 0.793960; second, 0.793811; third, 0.793639; fourth, 0.793582; fifth, 0.793576; sixth, 0.793561; seventh, 0.793499. This last weighing, although reached here for the second time (see above), must be received with doubt, because it is not in accord with the other elements of its series.

When these results are carefully examined it will be seen that with better apparatus and better management, the results of the former investigations were not quite reached. If 0.000338 be the specific gravity value of 0.1 per cent. in alcoholic strength, then the former results, which reduced the specific gravity from about 0.793824 to 0.793500, or 0.000324, indicated a difference in strength of 0.09585 per cent.

Taking the mean of three trustworthy readings of this paper, namely 0.793549, 0.793576 and 0.793561, which mean is 0.793562, and subtracting it from the original alcohol, 0.793824, the difference is 0.000262 and this is equivalent to 0.07751 per cent.

The writer was unable to carry through the design of this paper for want of time and leaves one or two methods of dehydration that have occurred to him, still untried, and he also very much regrets having to leave, for the present, a thorough repetition of the former successful process of nine years ago. It seems to the writer very certain that up to the present time no really anhydrous alcohol has been obtained, and therefore with the

present better apparatus and management, and especially by prolonged contact with the lime, through the old process, better results might reasonably be expected.

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## PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.

By WALTER D. FIELD.

Received June 17, 1893.

### PART I.

BY the term pyroxylin is understood the soluble nitric ethers of cellulose, namely, the di, tri, tetra, and penta-nitrates. From the date of the use of pyroxylin in photography by Scott Archer in 1851, the number of its uses has increased until, at the present time, tons of the lower nitrates of cellulose are produced yearly. With this increase of production improved methods of manufacture have been evolved.

So general has become the use of this material that to-day it is to be found everywhere. In the form of celluloid it is before us constantly. As a varnish it is used on penholders, pencils, silver and brass ware. Articles are bronzed with it as a medium. An artificial leather has been produced with it, many thousands of yards of which have found a ready market. These applications are all made, with the exception of celluloid, by the use of a solution of pyroxylin.

The first part of this paper pertains to the fibers and their selection for the purposes of nitration; the second part to the processes used for nitrating. The third and fourth parts will treat of the various methods of washing and drying the pyroxylin and of its solvents and uses.

*Selection of the Fiber.*—Cotton fiber, wood fiber, and flax fiber in the form of raw cotton, scoured cotton, paper, and rags are most generally used and give the best results. The fibers differ greatly in their manner of nitrating, a difference due undoubtedly to their physical structure; hence a given fiber demands a method of nitrating suitable for that particular fiber.

The cotton fiber is a flattened hollow ribbon, or collapsed cylindrical tube, twisted a number of times, and closed at one

end to form a point. The central canal is large and runs nearly to the apex of the fiber. Its side walls are membranous.

In regard to the influence of the structure of the cotton on nitration, F. Nettlefold (*Chemical News*, 55, 306) says: "It will be readily understood that the thin side wall tubes of the cotton fibers are readily penetrated by the mixed acids, and, consequently, the highest nitration results."

Wolfram (*Ding. Poly. Jour.*, 230, 45) says: "Concentrated acids give with cellulose from various sources the same final product, but dilute acids nitrate under the same conditions—cotton the most readily, then hemp, paper, straw, and linen."

Hardwich (*Manuel Phot. Chem.*, 136) recognizes the varying effects produced by the same strength of mixed acid on different fibers. He ascribes this difference to a difference in composition of the fiber and not to a difference in structure. In this conclusion he was undoubtedly wrong.

In the flax fiber the walls are comparatively thick, the central canal small; hence it is to be presumed that the nitration must proceed more slowly than in the case of cotton, which has large central canal and thin walls. The New Zealand flax gives the most perfectly soluble nitrates of any of the flaxes.

Hardwich (*loc. cit.*) says: "When a rather concentrated nitro-sulphuric acid is used cotton gives a glutinous collodion and calico a fluid collodion. In another acid weaker than the first the cotton succeeds well while the calico dissolves instantly. The difference in the action appears to depend principally on the thickness of the fiber. Calico produces pyroxylin of the fluid kind and is partially dissolved because the nitric acid in acting on the outside portion of the closely twisted fiber is reduced in strength, and hence the interior of the fiber is left more nearly in the condition of zylodine." By closely twisted fiber Hardwich refers to the thread from which the fabric is woven, and with this understanding his explanation of the action of the acids is clear.

One of the largest manufacturers of pyroxylin for the industrial arts uses the "Memphis Star" brand of cotton. This cotton is an upland cotton and its fibers are very soft, moist, and elastic. Its color is a light creamy white. This color is re-

tained by the cotton after nitration. The staple is short, and the twist inferior to other grades, the straight, ribbon-like filaments being quite numerous. They use this cotton carded, but not scoured. This brand of cotton contains a large quantity of half and three-quarter ripe fiber, which is extremely thin and transparent, distributed throughout the bulk of the cotton (Monie, *Cotton Fiber*, 67). This is a significant fact when it is known that from this cotton an extremely soluble pyroxylin can be produced.

Pyroxylin of an inferior grade, as regards color only, can be produced from the cotton wastes of the trade. These wastes are scoured, which renders them clean and suitable for nitrating. Paper made from the pulps of the sulphite and sulphate processes is capable of yielding a very soluble pyroxylin. It can be nitrated at high temperatures and still yield an increase in weight. The manufacturers of celluloid in this country use a tissue paper made of the flax fiber, and two to three one-thousandths of an inch in thickness. The paper is cut into squares of about one inch before nitrating.

Mowbray (United States patent No. 443,105, Dec. 3, 1890) says that a pure cotton tissue paper less than one five-hundredth of an inch in thickness, thin as it is, takes on a glutinous or colloid surface and thus requires some thirty minutes or thereabouts to enable the immersion to take place. With a thicker paper only the surface of the paper would be nitrated and the body of the paper would be unacted upon.

Mowbray (U. S. patent No. 443,105) recognizing the importance of the structural form of the cellulose on the nitrating process, uses a fiber which has been saturated with a solution of nitrate of soda, then dried slowly, claiming that the salt crystallized in the fiber or enters by the action termed osmose and opens up the fiber to the action of the acid bath. He also says he may use "any salt crystallized, or water crystallized by freezing in the cells of fibrose cellulose." Such a preparation of the fiber is not at all necessary when using a high temperature for nitrating. It might yield with some cottons a very soluble pyroxylin, when low nitrating temperatures are used. H. De. Chardonnet (English patent No. 19,560, 1891) heats the cellu-

lose intended for nitration to about  $150^{\circ}$  C. and claims to increase the solubility of the subsequently formed pyroxylin. The heating of the cellulose could have had no other effect than that of drying the fiber before nitration, and hence a pyroxylin more perfectly soluble in the ethereal solvents he was using in his testing.

Henly and Spill (English patent No. 1017, 1870) use "esparto grass in a finely divided condition (which is the novel and indispensable condition of the operation)."

Dietz and Wayne (U. S., patent No. 133,969, 1872) use ramie, rhea, or China grass, for producing a soluble pyroxylin and say in regard to it that "Pyroxylin made from ramie will always be of uniform strength and solubility. In making collodion from this pyroxylin a much smaller quantity of solvent is required than for pyroxylin made from cotton." It is to be doubted that ramie will yield a more soluble pyroxylin than cotton. The author's experience is entirely to the contrary.

Such is the influence of the physical form of the fiber on the process of nitration that when flax fiber and cotton fiber are nitrated with acid mixtures of exactly the same strength, and at the same temperature the solution of the first is glutinous or thick and the second fluid or thin. By simply nitrating at a higher temperature than the cotton, the flax will yield a pyroxylin giving an equally fluid collodion.

The presence of chlorine in the fiber must be carefully avoided

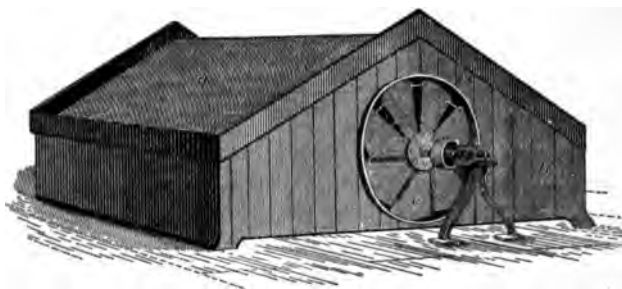


FIG. 1.

as such a fiber will yield a pyroxylin which is acid and which cannot be washed neutral.

The removal of all moisture from the fiber previous to nitra-

tion is essential to the production of a carefully prepared pyroxylin. This drying is best carried out on the form of drier used in drying wool. The plan of such a drier is given in Fig. I. The surface *a* is covered with wire cloth, having a half inch mesh, and should be galvanized.

Heater coils can be placed within the frame *b* and the hot air forced through the fiber by means of the rotary fan *c*.

If the fiber is found to need scouring to make it fit for the process of nitration, it is best scoured by those who make a business of this branch. Absorbent cotton is produced on such a large scale at the present time, that the manufacturers will sell it at a very low figure, in order to keep their plants in operation. The author obtained the fiber used by him for several years from this source.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, No. 6; SENT BY H. W. WILEY].

### THE PREDOMINANT ORGANIC ACID IN SORGHUM JUICE.<sup>1</sup>

BY OMA CARR.

Received June 1, 1903.

**I**N the work of the Department of Agriculture during the past few years attention has often been called to peculiarly tenacious and difficultly soluble incrustations forming upon the tubes of the evaporating apparatus of the sorghum-sugar houses of Kansas. Owing to the formation of these incrustations and the difficulty of removal the processes of manufacture are greatly impeded. Dr. Wiley collected a large amount of this scale at Medicine Lodge and directed me to make a study of its composition and properties. The following paper gives the results of a brief study of the scale.

The scale examined was in pieces of varying sizes, retaining the contour of the tubes from which it had been removed. A quantity of fifteen pounds was taken from some three hundred pounds forwarded from the factory at Medicine Lodge. The scale as prepared for examination consisted of a powder sufficiently fine to pass an eighty mesh sieve.

The analyses of two samples of the scale, one designated

<sup>1</sup> Read before the Chemical Society of Washington, May 11, 1903.

"Special," selected by Dr. Wiley for its size and cleanliness, and "Ordinary," representing the whole quantity removed, gave the following results :

	"Special."	"Ordinary."
Moisture.....	13.31 per cent.	14.21 per cent.
Magnesium oxide.....	15.93 " "	17.70 " "
Calcium oxide .....	7.27 " "	9.80 " "
Carbon dioxide .....	0.29 " "	2.76 " "
Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> .....	6.22 " "	4.10 " "
Silica .....	2.72 " "	1.75 " "
Organic.....	54.40 " "	49.31 " "
Undetermined .....		0.37 " "
	<hr/> 100.14 " "	<hr/> 100.00 " "
Carbon.....	23.67 " "	22.29 " "
" per cent. of organic	43.51 " "	45.20 " "

These data call for no special comments, aside from noting that the common scale has lain long enough for the absorption of considerable carbon dioxide, and that the elimination of this constituent would secure a greater uniformity between the two samples.

*Solubility.*—The ground material, one gram in quantity, was boiled an hour and a half with fifty cc. of the solvent, filtered hot upon a weighed asbestos film in a Gooch crucible, washed with alcohol and ether, dried at 105° and weighed. For this determination the "Special" sample was used, and it may be assumed that the slightly different composition of the two samples would cause but slight variation in the results.

Solvent.	Per cent. soluble.	Per cent. Inorganic insoluble.	Per cent. Organic insoluble.
2 per cent. HCl .....	95.67	2.85	1.48
5 " " " .....	95.00	2.78	1.32
10 " " " .....	95.97	2.60	1.43
20 " " " .....	95.87	2.59	1.54
Mean.....	95.85	2.70	1.45
2 per cent. H <sub>2</sub> SO <sub>4</sub> .....	94.48	3.67	1.85
5 " " " .....	95.81	2.56	1.63
10 " " " .....	95.85	2.74	1.41
*20 " " " .....	81.03	16.29	2.68
Mean.....	91.79	6.32	1.89
** " (2nd) .....	95.38	2.99	1.63
2 per cent. NaOH .....	67.15	21.58	11.27
5 " " " .....	62.45	24.68	12.87
10 " " " .....	59.85	29.47	10.68
20 " " " .....	60.35	26.29	10.20
Mean.....	62.45	26.29	11.26

\*Boiled only one hour.

\*\*Omitting the twenty per cent. determination.



tion is essential to the production of a carefully prepared pyroxylin. This drying is best carried out on the form of drier used in drying wool. The plan of such a drier is given in Fig. I. The surface *a* is covered with wire cloth, having a half inch mesh, and should be galvanized.

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Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> .....	6.22 " "	4.10 " "
Silica.....	2.72 " "	1.75 " "
Organic.....	54.40 " "	49.31 " "
Undetermined.....		0.37 " "
	100.14 " "	100.00 " "
Carbon.....	23.67 " "	22.29 " "
" per cent. of organic	43.51 " "	45.20 " "

These data call for no special comments, aside from noting that the common scale has lain long enough for the absorption of considerable carbon dioxide, and that the elimination of this constituent would secure a greater uniformity between the two samples.

*Solubility.*—The ground material, one gram in quantity, was boiled an hour and a half with fifty cc. of the solvent, filtered hot upon a weighed asbestos film in a Gooch crucible, washed with alcohol and ether, dried at 105° and weighed. For this determination the "Special" sample was used, and it may be assumed that the slightly different composition of the two samples would cause but slight variation in the results.

Solvent.	Per cent. soluble.	Per cent. Inorganic insoluble.	Per cent. Organic insoluble.
2 per cent. HCl.....	95.67	2.85	1.48
5 " " ".....	95.00	2.78	1.32
10 " " ".....	95.97	2.60	1.43
20 " " ".....	95.87	2.59	1.54
Mean.....	95.85	2.70	1.45
2 per cent. H <sub>2</sub> SO <sub>4</sub> .....	94.48	3.67	1.85
5 " " ".....	95.81	2.56	1.63
10 " " ".....	95.85	2.74	1.41
*20 " " ".....	81.03	16.29	2.68
Mean.....	91.79	6.32	1.89
** " (2nd).....	95.38	2.99	1.63
2 per cent. NaOH.....	67.15	21.58	11.27
5 " " ".....	62.45	24.68	12.87
10 " " ".....	59.85	29.47	10.68
20 " " ".....	60.35	26.29	10.20
Mean.....	62.45	26.29	11.26

\*Boiled only one hour.

\*\*Omitting the twenty per cent. determination.

It is seen from these results that hydrochloric acid has the highest solvent power of the three tried. Subtracting the organic insoluble from the total insoluble, the difference corresponds almost exactly to the per cent. of silica, showing that, aside from the small percentage of organic matter, the hydrochloric acid dissolves every thing but the silica. It is notable that the solvent power of hydrochloric acid depends very little upon its concentration.

The sodium hydroxide dissolves less than either acid, its power decreasing with increase of concentration. The portion insoluble in sodium hydroxide contains no silica.

In cleaning incrustated tubes, the above results, as well as good practice, suggest a procedure in which the use of hydrochloric acid precedes that of the lye.

As the work on the scale was done principally with the view of isolating and distinguishing the chief organic acids present, the following plan was pursued :

Finely divided scale (passing eighty mesh) was added to boiling sulphuric acid in ten per cent. solution until solvent action ceased and filtered hot, the filtrate being perfectly clear and transparent. The filtrate was cooled and two volumes eighty per cent. alcohol added. The calcium and magnesium sulphates precipitated were removed by filtration. The alcohol was expelled from the filtrate and the latter considerably reduced in volume by evaporation. There was added now a very strong alcohol (five volumes) and the white precipitate allowed to settle. It was decanted and washed with alcohol. The precipitate was purified by dissolving in water and repeated reprecipitation by alcohol. Finally from the solution in water free of carbon dioxide it was precipitated with a carbon dioxide-free solution of acetate of lead. This product was purified by repeated decomposition with hydrogen sulphide and reprecipitated with lead acetate. The final precipitation yielded my salt (I), or "scale salt," the combustion of which gave:

	Per cent.
Carbon .....	13.884
Hydrogen .....	1.210
Lead .....	58.420
Oxygen (difference) .....	26.486
	<hr/>
	100.000

The salt contained 2.46 per cent. moisture, eliminating which would give the following numbers :

	Per cent.
Carbon .....	14.23
Hydrogen .....	0.94
Lead .....	62.11
Oxygen .....	22.72
	<hr/>
	100.00

These figures correspond to the formula :

(C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>)<sub>3</sub>Pb<sub>3</sub>, or tri-plumbic citrate.

After digestion with sulphuric acid the insoluble residue, undried and unwashed, subjected to analysis, gave the following numbers :

	Per cent.
Moisture .....	6.83
Calcium oxide.....	13.92
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	1.70
Silica .....	4.26
SO <sub>3</sub> .....	62.43
Organic .....	10.47
Undetermined.....	0.39
	<hr/>
	100.00

The SO<sub>3</sub> present was combined, twenty per cent. with calcium (42.77 per cent. sulphate), and 1.98 per cent. with the Fe and Al (3.88 per cent. sulphates). The rest was free H<sub>2</sub>SO<sub>4</sub>. Eliminating the SO<sub>3</sub> we have :

	Per cent.
Moisture .....	18.18
Calcium oxide.....	37.05
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	4.52
Silica .....	11.34
Organic .....	27.87
Undetermined.....	1.04
	<hr/>
	100.00

Reducing to a water-free basis these data become :

	Per cent.
Calcium oxide.....	45.28
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	5.52
Silica .....	13.86
Organic .....	34.06
Undetermined.....	1.28
	<hr/>
	100.00

Reducing original scale to water-free substance and comparing its analysis with that of the residue after digestion we have :

	Original.		Residue.	
Magnesium oxide .....	20.63 per cent.		....	
Calcium oxide .....	11.41	"	45.28 per cent.	
Carbon dioxide.....	3.22	"	....	
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	4.78	"	5.52	"
Silica .....	2.04	"	13.86	"
Organic .....	57.48	"	34.06	"
Undetermined .....	0.43	"	1.28	"
	<hr/>		<hr/>	
	100.00	"	100.00	"

The silica having remained unaffected by the digestion, we may place the residue on the same plane as the original material by decreasing the percentages in the residue in the ratio of the respective percentages of silica. Analyses so corrected are as follows, calculated to water-free substance :

	Original.		Residue.	
Magnesium oxide. ....	20.63 per cent.		....	
Calcium oxide.....	11.41	"	6.66 per cent.	
Carbon dioxide.....	3.22	"	....	
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	4.78	"	0.81	"
Silica .....	2.04	"	2.04	"
Organic .....	57.48	"	5.01	"
Undetermined.....	0.43	"	0.13	"
Removed .....	....		85.35	"
	<hr/>		<hr/>	
	100.00	"	100.00	"

The organic matter has fallen from 57.48 per cent. to 5.01 per cent., 52.47 per cent. being removed, together with 20.63 per cent. MgO. Dividing the per cent. of the removed organic matter by the molecular weight of both aconitic and citric acid, we have :

$$\begin{aligned}
 52.47 \div 210 &= 0.25 = \text{citric} \\
 52.47 \div 174 &= 0.301 = \text{aconitic} \\
 20.63 \div 120 &= 0.172 = \text{MgO} \\
 20.63 \div 100 &= 0.206 = 2\frac{1}{2} \text{ MgO}
 \end{aligned}$$

As, however, the organic matter of the water-free original material contained 45.19 per cent. carbon, and as citric acid contains but 37.7 per cent., other organic matters are present containing the difference between 45.19 per cent. and 37.7 per cent., or 7.49 per cent. Correcting the decimal given for citric

acid (0.205) by the equation  $45.19:37.7::0.205:x$ , we find  $x$  to equal 0.171, or practically identical with the decimal for  $3\text{MgO}$ .

Aconitic acid contains 41.84 per cent. carbon, and correction of the decimal by substitution of 41.48 for 37.7 in above equation brings the decimal to 0.278.

#### ACETIC ACID DIGESTION.

As with sulphuric acid, in this digestion the scale was added to boiling acid, the solution being arrested before discoloration commenced. The lead salt was prepared in the manner described for sulphuric acid, due precautions being taken to prevent formation of lead carbonate. Combustion of this salt resulted as follows:

##### Salt II (acetic acid digestion).

Carbon .....	13.03 per cent.
Hydrogen.....	1.74 "
Lead.....	57.69 "
Oxygen (diff.) .....	27.54 "
	<hr/>
	100.00 "

The salt contained 7.50 per cent. moisture, eliminating which we have:

	Salt II.	Theory tri-plumbic citrate.
Carbon .....	14.09 per cent.	14.42 per cent.
Hydrogen .....	0.89 "	1.00 "
Lead .....	62.37 "	62.15 "
Oxygen .....	22.65 "	22.43 "
	<hr/>	<hr/>
	100.00 "	100.00 "

It would appear that this salt has slightly oxidized in drying. After digestion the insoluble residue contained:

		Moisture free.
Moisture.....	11.84 per cent.	....
Magnesium oxide.....	16.63 "	18.98 per cent.
Calcium oxide .....	9.74 "	11.05 "
$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ .....	2.43 "	2.72 "
Silica .....	2.39 "	2.71 "
Organic.....	54.26 "	61.54 "
Undetermined .....	2.72 "	3.00 "
	<hr/>	<hr/>
	100.00 "	100.00 "
Carbon .....	19.49 "	22.11 "
Carbon per cent. of organic matter .....	....	35.93 "

From an equal weight of material much less of the lead salt was secured from the acetic acid digestion than from the sulphuric acid preparation.

For the purpose of comparison a pure tri-plumbic citrate was prepared, the combustion resulting as follows:

Salt III (tri-plumbic citrate).	
Carbon .....	13.96 per cent.
Hydrogen .....	1.33 "
Lead.....	59.76 "
Oxygen (diff.) .....	24.95 "
	<hr/>
	100.00 "

The salt contained 3.59 per cent. moisture, elimination of which produces the following numbers:

		Theory tri-plumbic citrate.	
Carbon .....	14.42 per cent.	14.42 per cent.	
Hydrogen .....	0.93 "	1.00 "	
Lead.....	61.98 "	62.15 "	
Oxygen .....	22.61 "	22.43 "	
	<hr/>	<hr/>	
	100.00 "	100.00 "	

The three lead salts, corrected for uncombined water, were grouped thus in the following table and compared with the theoretical salt:

- (I) From sulphuric acid digestion.
- (II) From acetic acid digestion.
- (III) Tri-metallic citrate of lead.
- (IV) Tri-metallic citrate of lead, theory.

	I. per cent.	II. per cent.	III. per cent.	IV. per cent.
Carbon ....	14.23	14.09	14.48	14.42
Hydrogen.....	0.94	0.89	0.93	1.00
Lead .....	62.11	62.37	61.98	62.15
Oxygen .....	22.72	22.65	22.61	22.43
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00

From the above it is apparent that the lead salts are unquestionably citrates.

For further proof the acid was freed of lead by hydrogen sulphide, excess of the precipitant removed, and in aqueous solution the following reactions were obtained:

- (I) With bichromate of potash, *coffee brown color*.
- (II) Boiled with strongly alkaline potassium permanganate gave *green color*.

(III) Heated at 100° C. for an hour with ten parts sulphuric acid, *lemon yellow color*.

(IV) Characteristic reaction of *precipitation when heated in aqueous solution*.

Parsons (*Am. Chem. J.*, 4, 39) gives the results of an examination of "scale from sorghum-sugar pans," and concludes that the "scale is a two-thirds metallic calcic aconitate (as this is a quotation we do not feel at liberty to change from Parsons' own words to "dicalcium aconitate") containing one molecule of combined water." Comparing Parsons' data with those obtained in these more recent researches it seems probable that the aconitic acid is a product formed in manufacture. The scale examined by Parsons was derived from pans in which the boiling was conducted under atmospheric pressure. The scale recently examined came from evaporators in which the boiling was done in vacuo. Inasmuch as citric acid when strongly heated loses one molecule of water and becomes aconitic according to the equation,  $C_6H_8O_7 - H_2O = C_6H_6O_6$ , it is probable that Parsons' scale formed under high temperature and prolonged heating may have suffered dehydration and become an impure calcium aconitate. It would appear also that the scale formed in the evaporating apparatus of sorghum-sugar houses contains little, if any, aconitate. At the same time it may be conjectured that the reported presence of aconitic acid in the refuse or final products of sugar cane houses, molasses, skimmings, etc., may be attributed to formation in the manufacturing processes and not to presence in the canes or juices.

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## A CRYSTALLINE CHROMIUM TUNGSTATE.

BY EDGAR F. SMITH AND HERMAN L. DIECK.

Received June 27, 1893.

POTASSIUM bichromate was brought together with an equivalent amount of pure tungstic oxide. Heat was applied to the mixture; fusion followed and the mass was held in this condition until the evolution of gas bubbles ceased. The temperature was never higher than necessary to maintain a liquid condition of the mixture. After cooling, the fused mass



was treated with water until the latter ceased to dissolve anything. Sodium hydroxide and ammonium hydroxide were next employed for washing purposes, and these finally displaced by pure distilled water. The well-washed substance was carefully dried at  $100^{\circ}$ . It showed a dark brown color, and when examined under the microscope revealed the presence of acicular, brown-colored crystals of orthorhombic outline; associated with these were green-colored crystals, which were apparently of the same crystallographic system. This mixture was exposed to the action of aqua regia for an hour; it was then filtered, washed, and dried. A re-examination of the brown residue showed that the green crystals had been removed and that the brown-colored body alone remained. It had been unaffected by the acid. Two weighed portions of the mixed crystals were treated with aqua regia, the acid solutions evaporated, the residues dissolved in water, and the aqueous solutions treated with ammonium hydroxide. Chromium hydroxide was precipitated. In the one case the ignited oxide equaled 2.89 per cent. and in the other 2.92 per cent. of the original mixture. A sufficient quantity of pure brown crystals was prepared for analysis. We first endeavored to effect their decomposition by fusion with sodium carbonate and sulphur. Several attempts demonstrated that this course offered little chance of a satisfactory analysis. Digestion with hydrofluoric acid gave a poor result; the acid failed to completely decompose the material. Portions of the substance were next ignited in a current of hydrogen, the residue then oxidized with aqua regia, evaporated to dryness and treated with ammonium hydroxide. Considerable tungsten was removed in this manner, but much remained with the chromium, from which it seemed almost impossible to free it. The mixture of tungstic and chromium oxides was ignited a second time in hydrogen and again treated with aqua regia. This operation was repeated until no more tungsten could be extracted. Combining the separate portions of tungstic oxide, their total quantity gave 88.37 per cent.  $\text{WO}_3$ . The chromium oxide, previously associated with this amount of tungstic oxide, equaled after careful purification, 11.75 per cent. This method of analysis having proved tedious and time-consuming, we de-

terminated to try fluxing the brown-colored material with a mixture of pure sodium carbonate and potassium nitrate, as we had previously satisfied ourselves that it did not contain the alkali metals. The fusion was taken up with water, acidulated with hydrochloric acid, and evaporated to dryness. Tungstic acid separated; the residue was moistened with acid and again evaporated. It was then digested with acid and left pure tungsten trioxide which was filtered, washed, and weighed. It equaled 88.08 per cent. The chromium oxide in the filtrate, after precipitation and purification, equaled 12.10 per cent. Upon repeating this course with new portions of the substance we obtained results that agreed with those just given, so that we feel satisfied that they represent the true composition of the brown crystals. Taking the mean of the percentages of the two analyses given above as a basis of calculation we deduce as the most probable ratio,  $1\text{Cr}_2\text{O}_3, .5\text{WO}_3$ , or  $\text{Cr}_2\text{O}_3, .5\text{WO}_3$ . The theoretical requirements of this formula are :

	Per cent.	
$\text{WO}_3$ .....	88.40	
$\text{Cr}_2\text{O}_3$ .....	11.59	
	Per cent. found.	
$\text{WO}_3$ .....	88.37	88.08
$\text{Cr}_2\text{O}_3$ .....	11.75	12.10

Tungstates of chromium that exist<sup>1</sup> are hydrous and have been prepared by double decomposition in the wet way. The salt we describe is, so far as we can ascertain, the first of its class.

UNIVERSITY OF PENNSYLVANIA,

June 15, 1893.

## THE METHODS OF TESTING FATS AND OILS.

By DR. ERNEST MILLIAU, DIRECTOR OF THE GOVERNMENT TESTING LABORATORY, MARSEILLES, FRANCE.

Read before the New York Section May 29, 1893.

THE difficulties of chemical analyses of fatty matters are greatly increased, not only by the slight differences which characterize the various glycerides, but also by the numerous cases of isomerism, and the phenomena of oxidation and fermentation which modify their molecular structures, the resins and the essen-

<sup>1</sup> *Fremy's Encyclopédie Chimique*, 3, 166.

tial oils which they contain, the foreign matters which spoil them, the composition of which varies infinitely, according to the nature of the soil from which the plant draws nourishment, the method of extraction, age, and a thousand other causes, needless to mention. Since the methods of communication have been facilitated and exchanges have become more numerous, the different markets of the world have been flooded with fatty matters presenting different characters, though of the same nature as those which industry and commerce have been accustomed to.

We have been led to seek methods of analysis for oils not by their impurities, which vary according to their origin, but by the examination of their principal constituents, which remain practically the same for the same species.

For example, it is now well known that the olive oil of Tunis, Morocco, and other provinces presents often the character of adulterated oils if analyzed without proper precautions or by old processes.

Accordingly most governments and large companies have modified their specifications. It is indispensable for obtaining precise results to submit the material to a purification, preceded and followed by a number of filtrations. By thus removing the impurities, which when present alter the results, we bring back the fatty bodies of the same species to a type which is always practically the same. To reach this end we work sometimes with washing by hot distilled water, sometimes by strong or dilute alcohol, sometimes we refine the fatty matter by the use of caustic soda lye, containing ten per cent. sodium hydrate, employed in the proportion of ten per cent. of the fat. The emulsion is poured upon a saturated solution of sodium chloride, and by the action of gentle heat, the different parts separate and the clear oil holding in suspension insoluble particles of soap rises quickly to the surface.

It is well to note that fatty matter, even when neutral, as has been demonstrated, dissolves notable quantities of alcohol, which must be eliminated if this method of washing has been employed. The nature of the operation can not be fixed definitely; it varies according to the nature of the impurities and the object

of the research. In determining the amount of volatile acids we must be contented with simple filtration and when examining the oils of the cruciferae we must not use caustic soda, which changes organic sulphur to soluble sodium sulphide. Having finished the preliminary operations we can, according to circumstances, operate directly on the neutral fat or the fatty acids prepared from it.

The fatty acids collected in the nascent state, that is to say when they rise to the surface in a pasty mass, have much stronger chemical affinities than when melted and dehydrated. This difference is particularly remarkable in the examination of cotton-seed and sesame oils, the black and red colorations obtained very clearly with a mixture of five per cent. upon the nascent fatty acids are not visible with the same fatty acids when melted.

That purification skillfully made does not destroy the chemical characters of the oil, is easy to verify by treating comparatively the same oil containing five per cent. of the fatty matter the presence of which we wish to demonstrate. The reactions of the added material are in general intensified by these different treatments.

By working upon the fatty acids of the neutral oils I have been able to demonstrate the purity of certain fatty matters which appeared adulterated and in which the presence of cotton-seed and sesame oils was indicated by the old processes, which I have been able to revise. (*Circulaire du ministre de la marine français, en date du 26 juillet, 1892. Rapport du Resident général de Tunisie, en date du 9 mai, 1892. Circulaires des ministres du commerce et de l'agriculture, etc.*)

I well know that in practice these preliminary operations may appear very tedious, but I do not advise their use except in cases where adulterations have been indicated by the usual methods, and it is desired to make the proof positive.

Besides I cannot understand why a chemist has always been expected in the analysis of such delicate materials as fats to discover an infallible reagent, a single drop of which will immediately turn olive oil green, arachide black, sesame red, etc., so that any inexperienced man could discover adulteration and

bring the perpetrator to justice. This requirement of the most difficult part of chemical verification, is absolutely incomprehensible and is only to be excused by the ignorance of those who ask it.

We will now proceed to the study of each oil in particular. We will pass rapidly over those which possess only a secondary interest so as to lay greater stress upon those which are the object of a great number of sophistications as for example, olive oil. But in the first place we will indicate rapidly the general processes physical and chemical which are used for the identification of the various fats.

#### GENERAL METHODS.

(1) *Specific Gravity*.—Is taken with accuracy by the Mohr balance, which is too well known to need description. It must be borne in mind that the specific gravity of the same fat varies greatly with individual samples, and this physical character is not sufficient to allow us to decide on purity or adulteration.

(2) *Action of Nitrous Fumes*.—We owe to a Marseilles gentleman, M. Poutet, the first serious process to recognize certain adulterations of olive oil. It was supposed especially to discover the presence of poppy-seed oil which at that time was a very frequent adulteration and for which the process gave good results.

It is based upon the transformation of the oleine to its isomeric modification elaidine by the action of nitrous fumes. It has been modified by other chemists, Messrs. Boudet, Fauré, and Cailletet. The process of M. Cailletet was most sure and simple and we use it in the following manner:

We take a tube ten cm. long, 2.5 cm. wide, in which are twenty cc. of the fat to be analyzed. Six drops of pure sulphuric acid at 66° B., are added, the tube shaken one minute, and then nine drops of nitric acid C. P. 40° B. are added, after which the tube is again shaken and then plunged in boiling water, where it is left exactly five minutes, after which it is cooled in a water bath at 8°–10° C., whence it is taken at the end of two hours, and the condition of the mass observed. It is well to note the different colorations obtained, first after the addition of the

sulphuric acid, second after the addition of nitric acid, third after removal from the water bath and fourth after chilling.

(3) *Sulphuric Saponification*.—M. Maumené proposed to observe the rise of temperature produced by rapidly mixing sulphuric acid with oil. The manner of applying the process in our laboratory is as follows: Fifty grams of the fat for analysis are weighed into a conical glass of 100 cc. capacity. The temperature is noted and ten cc. sulphuric acid 66° B. at the same temperature as the oil is added. The two liquids are stirred together for one minute. An accurate thermometer is then immersed in the upper portion of the mass, stirred slowly, and the maximum temperature noted. The initial temperature must be at least 20° C. In order to obtain exact results it is well to make several determinations and take their mean when the variation does not exceed 2° C.

To obtain the relative sulphuric saponification, we note the rise of temperature obtained with fifty grams of distilled water at the same temperature as the oil and ten cc. of the same sulphuric acid. The number of degrees obtained by the oil is multiplied by 100 and the product divided by the number of degrees obtained with water. This process has the advantage of giving results, nearly constant, with acids of somewhat different strength. I have tried the application of the sulphuric saponification with semi-solid vegetable oils by working at 2°–3° above their melting points, and the results have been very satisfactory, especially for palm-nut and cocoanut oil, because the differences between them and the fluid oils often amount to 45° or more,—as between palm-nut oil and sesame oil, for example.

(4) *Iodine Number*.—In the fatty bodies there are members of unsaturated series, as for example oleic acid, which can absorb into its molecule as many atoms of the halogens as there are lacking atoms of hydrogen for complete saturation.

The iodine number of olive oil varies between eighty and eighty-four, that of arachide or peanut oil is ninety-seven, while that of cotton-seed oil is 108. These differences then allow, within certain limits, the determination of the purity of the various fats. We apply the Hubl method as follows:

**Solutions required :**

	Grams per liter.
Alcoholic solution of iodine.....	50
Solution of sodium thiosulphate.....	24.8
“ “ mercuric chloride.....	60
“ “ potassium iodide .....	100

Five (5) grams of fatty acids are weighed out, diluted to 100 cc. with ninety-two per cent. alcohol, ten cc. of the solution are taken, and to it added twenty cc. of the iodine solution and fifteen cc. to twenty cc. of the solution of mercuric chloride. The flask is closed and allowed to stand three hours. Twenty cc. of the potassium iodide solution is added and the excess of iodine titrated. When the brown coloration begins to disappear a few drops of starch solution are added and then thiosulphate until the color disappears.

We will pass in silence the other indices, such as that of acetyl, which is of use only to discover castor oil.

(5) *Freezing Point*.—The freezing point is easy to determine by means of a thermometer and a freezing mixture.

(6) *Melting Points of Fatty Acids*.—The dry and melted fatty acids are sucked into a capillary tube. After solidification the tube is placed beside the bulb of a sensitive thermometer and immersed in a beaker of water, the temperature of which is raised very slowly. The reading of the thermometer is taken the instant the body passes from the solid to the liquid state.

(7) *Solidification Point of Fatty Acids (Titer)*.—The dried and melted fatty acids are placed in a tube fifteen cm. long and two cm. in diameter, which is suspended in a wide-mouthed bottle with a perforated stopper. A thermometer graduated to tenths is inserted so that the bulb reaches the center of the material. At the moment solidification commences a circular movement is given to the thermometer, stirring the whole mass; the thermometer is then left at rest and carefully watched till the mercury ceases to rise, the reading then taken gives the point of solidification or titer conventionally adopted.

(8) *Saturation*.—We operate on five grams of the melted and dried fatty acid with a solution of normal caustic soda. The number of cc. absorbed gives the saturation number.

(9) *Solubility in Absolute Alcohol*.—We determine this in the

following manner: The fat is neutralized by agitating in a closed separating funnel for thirty minutes with twice its weight of ninety-five per cent. alcohol; after settling it is drawn off and the alcohol held in solution driven off at low temperature, after which it is agitated at  $15^{\circ}$  C. or at a few degrees above the melting point, if solid at  $15^{\circ}$  with twice its weight of absolute alcohol. A known quantity of this alcohol is evaporated, the residue weighed, and the quantity of oil dissolved by 1,000 grams of alcohol is calculated.

#### FLUID VEGETABLE OILS.

*Olive Oil.*—Olive oil, like other vegetable oils, is a mixture of neutral glycerides, oleine, stearine, palmitine, etc., and a variable quantity of free fatty acids. It is the edible oil *par excellence*, and the south of France owes a portion of its prosperity to the cultivation of the olive tree. This culture is to-day almost precarious in certain countries, though the consumption continually increases, and olive oil always enjoys the just title of uncontested superiority. We can only attribute these remarkable results to the adulterations made for the purpose of selling under the name of olive oil, seed oils, or adulterated olive oil. We would be easily freed from these adulterations if chemists had at their disposition absolutely sure means to recognize them. Unfortunately the similarity of composition and reaction of the various vegetable oils render the demonstration of their presence extremely difficult. In face of the prejudice caused by adulteration the greatest efforts have been made to solve the problem, and although the results have not been sterile, they have not yet reached a satisfactory solution. It is necessary to say that if certain adulterators succeed in selling seed oils disguised as olive, they reverse the problem for the chemist by making him seek olive oil in seed oil. I may remark that the fraud is not always so great; very often the proportion of seed oil is not higher than ten per cent. Consequently for our method of analysis to be considered absolutely good it must give results, without recourse to comparisons, which satisfactorily show five per cent. in a mixture. Under these conditions we are certain to discover adulteration when made in the proportion of ten per cent.



Let us rapidly review the general processes for the recognition of peanut, sesame, cotton-seed, and poppy oils in olive oil, and we must acknowledge that none of them demonstrate less than ten per cent.

*Specific Gravity.*—The specific gravity of olive oil varies from 0.915 to 0.918. We have 0.917 to 0.918 for undecorticated peanut, 0.921 for decorticated peanut, 0.923 for sesame, 0.921 to 0.924 for cotton-seed oil, 0.924 for poppy oil. These variations of density in the olive oil do not allow us to recognize a mixture with any degree of certainty.

*Action of Nitrous Fumes.*—When taken from the water bath, if the oil contains a fairly large proportion of peanut oil, it will appear wine red. Pure olive oil is, on the contrary, lemon yellow. When taken from the cold bath a complete solidification is observed with pure olive oil, which has the appearance of very light fresh butter. With a mixture of fifteen per cent. of all other oils there is no solidification. This method gives good means of detecting peanut and poppy oils in edible, but is of less use when applied to oils used for industrial purposes, which may not solidify though pure.

*Sulphuric Saponification.*—The rise of temperature of olive oil is 35°, the relative 94°. A rise of temperature above 35° usually indicates adulteration. Equal or lower results do not absolutely indicate purity because certain pure olive oils give only 31°, 32°, and 33°, and in consequence after the addition of seed oils show only 34°-35°.

*Indices.*—The iodine number varies from eighty to eighty-five, and in a certain measure helps us to discover seed oils. It likewise offers us a quantitative method with a mixture of known oils. The variation in composition of the same oil spoils its sensitiveness for determining mixtures from five to ten per cent.

We will not mention the other general processes, but will dwell particularly on the special reactions which characterize the presence of the three oils most frequently used to adulterate olive oil, to wit, peanut, sesame and cotton-seed.

These processes have a much greater analytical value than the general ones; for if in the course of analysis we find unsatis-

factory results with the latter, we can detect adulterations with certainty by the former.

*Examination for Peanut Oil.*—The density is almost the same. The sulphuric saponification, and above all the Cailletet process give us good results, but only the presence of arachidic acid  $C_{22}H_{44}O_2$ , melting point  $75^\circ$ , allows the sure recognition of the presence of peanut oil. We have adopted with slight modifications the method of Renard. Twenty grams of the oil are saponified by 20 cc. of a caustic soda solution  $36^\circ$  B., diluted in 100 cc. alcohol ninety per cent. The soap formed is precipitated by a fifty per cent. solution in alcohol of lead acetate, which must be neutral. After complete precipitation decant while warm and wash the residue with alcohol, which after being ground in a mortar is agitated with 200 cc. of ether. This operation is repeated three times to remove the last traces of lead oleate, soluble in ether. The residue is then put in a porcelain dish containing two or three liters of distilled water and fifty cc. hydrochloric acid. When decomposition is completed the solution is decanted and the fatty acids washed with distilled water, after which they are dried in an oven to remove the last traces of water, when they are dissolved in forty cc. of ninety per cent. alcohol. A drop of hydrochloric acid is added, and the mixture chilled to  $15^\circ$ . Peanut oil gives a generous deposition of arachidic acid crystals. These are washed twice, using twenty cc. each time of ninety per cent. alcohol, then three times with twenty cc. each time of seventy per cent. alcohol, in which arachidic acid is completely insoluble. The washing is complete when a few drops give no residue on evaporation. The acids are warmed slightly and treated with boiling absolute alcohol. After filtration the alcohol is evaporated in the oven at  $100^\circ$  till the weight of the residue remains constant. If the melting point of the residue is between  $73^\circ$  and  $75^\circ$  we can affirm the presence of peanut oil. We must be sure of the freedom of the fatty acids from all traces of oleic acid, which prevents their crystallization. This elaborate but truly scientific process must be carried out only by skilled hands.

*Examination for Sesame Oil.*—To recognize sesame oil in olive oil we can use the specific gravity, the sulphuric saponifi-

cation and Cailletet process, but especially the method which we use in our laboratory, and which consists of the reaction of hydrochloric acid and sugar upon the fat.

We do not operate on the glyceride, but on the derived fatty acids. If the oil is operated on directly we can obtain a red or pink coloration with a perfectly pure olive oil. I have frequently observed this coloration in my laboratory with olive oils from Tunis, Algiers, Molfetta, Bitonto (Italy), and more rarely with those from Provence. This coloration comes from the coloring matter dissolved in the juice which flows out along with the oil from the presses. This can be shown by treating the separated juice with hydrochloric acid and sugar with which it gives a coloration exactly resembling that given by sesame oil. It is, therefore, of the highest importance to work with pure fatty acids according to the process I am about to describe and which has been called the Milliau process.

*Method of Operating.*—We saponify fifteen cc. of the fat under examination with ten cc. of the solution of caustic soda,  $36^{\circ}$  B., with the addition of ten cc. ninety-two per cent. alcohol. When the boiling mixture becomes clear we add 200 cc. hot distilled water and boil to expel the alcohol. Then decompose with ten per cent. sulphuric acid. The fatty acids are removed from the surface in the pasty state, washed by shaking in a test tube with cold distilled water, after which they are heated in an oven to  $105^{\circ}$ . When the greater part of the water is eliminated and they commence to melt, we pour them on half their volume of pure hydrochloric acid which has been saturated in the cold with finely pulverized sugar. The mixture is shaken violently in the test tube. The presence of sesame is always distinctly indicated by the rose or red coloration of the acid solution. Other oils leave the acid colorless or communicate to it a slightly yellowish tinge. This reaction is extremely delicate and permits the sure recognition of the presence of one per cent. of sesame oil, not only in olive oil, but in all fatty mixtures as well as in soap.

This process was presented before the Academy of Sciences by M. Debray, February 20, 1888, and was awarded the gold medal by the Société d'Encouragement (Report of M. Muntz in the name of the Agricultural Committee, February 20, 1889).

*Examination for Cotton-Seed Oil.*—Till recently the detection of cotton seed in olive oil was considered impossible, and accordingly the different scientific societies and several chambers of commerce promised great prizes to the inventor of a process which would detect this adulterant. Two simultaneous methods were proposed, one by an Italian savant, M. Bechi, the other by myself. These two processes, which at first sight appear quite analogous and based upon the same reaction, differ completely from the scientific standpoint as well as in the exactness of the results obtained. M. Bechi has based his process upon the direct action of silver nitrate upon the oils. As long ago as 1878 we made some experiments with M. Puget of a similar nature, and the uncertainty of the reactions led us to abandon them entirely. M. Bechi's process possesses the serious inconvenience of causing us at times to reject, as adulterated, oils which are absolutely pure, and thus work injustice and create a considerable prejudice against the firms which have sold them. From results obtained at L'Institut National Agronomique de Paris as well as in other laboratories a deep coloration has been found with oils absolutely pure. Outside of these inconveniences, which are sufficient to cause us to throw it aside, it has the defect of being based upon a coloration having no well-defined chemical character, and it produces effects with different substances the action of which it is impossible to explain. The use of colza oil has the serious fault of bringing into the reaction a second oil which may be impure and completely nullify the results. Finally, the conclusions reached by the Italian scientific commission instituted at Rome by act of the ministry to study the Bechi process show that it is not certain on quantities of less than fifteen per cent. It solves the problem of finding less than ten per cent. no better than the Cailletet process, which shows the presence of fifteen per cent. The same commission declared also that olive oil containing glycerine, free fatty acid, formic and acetic acids, does not give a sure reaction with the Bechi reagent. Since all olive oils contain free fatty acid from several tenths of one per cent. for virgin oil to 100 per cent. in some industrial oils, what conclusions can we arrive at?

The Bechi process will give, from fifteen per cent. up, a brown

coloration of variable intensity. But in oil containing cotton-seed oil, which is fresh and well-refined, the only sort used for edible purposes, we have a very weak reaction; while with an olive oil perfectly pure, but containing organic or mineral matters in suspension or solution which have an action upon the reagents, we would have a pronounced coloration. That is why I gave up these uncertain and variable results obtained in 1878 and studied the action of nitrate of silver, not upon the oil itself, but upon the products of saponification derived from it. The results obtained exceeded my expectations and have been published by the press as the Milliau process.

*Milliau Process, Mode of Procedure.*—In a porcelain dish of 250 cc. capacity fifteen cc. of the oil to be investigated is heated to about  $110^{\circ}$ ; a mixture of ten cc. of a solution of caustic soda at  $36^{\circ}$  B., and ten cc. of alcohol at  $90^{\circ}$  B. is then slowly poured on the oil. When the mass boils it becomes clear and homogeneous; 150 cc. of hot distilled water is added and boiling continued to expel the alcohol. The fatty acids are displaced with ten per cent. sulphuric acid solution added in slight excess, and the pasty acids immediately collected with a small platinum spoon. They are washed by shaking several times in a test tube with an equal volume of cold distilled water, the drops of water are drained off and they are then poured into a tube 2.5 cm. in diameter and nine cm. long; fifteen cc. of alcohol, ninety-five per cent., and two cc. of three per cent. nitrate of silver solution are added. The tube is protected from the light in a water bath at  $90^{\circ}$  C. till about one-third of the alcohol is expelled, which is replaced by ten cc. distilled water. The heating is continued a few minutes and the coloration of the insoluble fatty acids is observed. The presence of cotton-seed oil in any proportion whatever causes a mirror-like precipitate of metallic silver, which blackens the fatty acid of the mixture.

The members of the agricultural committee, composed of the greatest savants of France, MM. Pasteur, Eug. Tisserand, Boitel, Chatin, Heuzé, Hardi, Rissler, Schloesing, Ronna, Lavalard, Müntz, Prillisux, Muret, Bon Chénard, Liebaut, after having tested the process on 128 samples from different provinces have had the kindness to confer upon me the gold

medal for this method of analysis, and I will take the liberty to present the conclusions of their secretary, M. Müntz, director of the laboratories of L'Institut National Agronomique: "The preliminary saponification applied to the examination of fatty matters constitutes a new method on which we can confidently rely, not only in the analysis of edible products, but besides of those used for industrial purposes, and also for soaps. It has for effect not only to give an extremely sensitive reaction, but it also eliminates accidental and secondary products which can mask the reaction and deprive it of precision. Feb. 1889."

It is of course well understood that the same processes can be used for the detection of peanut, sesame, and cotton-seed oils in all other fatty mixtures.

*Peanut Oil.*—Peanut oil apart from the arachidic acid which it contains presents no special characters.

*Sesame Oil.*—The purity of sesame oil may be demonstrated by shaking ten cc. of oil, first with five drops of sulphuric acid at 53° B., then with five drops of nitric acid at 28° B. The oil undergoes a progressive change of color, through various shades from light-green to red; the final red coloring matter obtained by this oxidation process turns yellow by the action of alkalies and returns to its original color with acids. This curious phenomenon does not take place with other oils, but is obtained sometimes when working on sesame oils slightly adulterated; besides the industrial oils from hot pressing may give, though pure, negative results. I have devised a rapid process, especially applicable for the recognition of castor oil in the industrial sesame oils.

*Millian Process.*—For the rapid identification of castor oil and sesame ten grams of the oil are shaken up with four drops of sulphuric acid at 66° B., a drop of nitric acid at 40° is added and shaken violently; pure sesame oil blackens immediately, while that containing castor oil remains turbid yellow.

*Cotton-seed Oil.*—From a chemical standpoint we have nothing particular to say. From the industrial point of view we may state that this product becomes more useful every day, that its cheapness allows everybody to use it, and this fat material daily augments its important place in the markets of the world.

We will go rapidly over the drying oils, poppy-seed, linseed, walnut, cameline, over those of the cruciferae, colza, rape, and mustard, as well as the oils of the sweet almond, hazel nut, and castor.

I will take the opportunity, however, to mention a rapid process which I have found for detecting the presence of castor oil in other oils. It is well known that the oils in general are soluble in petroleum ether, while castor oil, which distinguishes itself by its solubility in alcohol is likewise remarkable for its insolubility in petroleum ether. Unfortunately this insolubility disappears at the ordinary temperature when castor oil is adulterated with a small proportion of a soluble oil.

It is only necessary to demonstrate its insolubility by shaking in a test tube one volume of the oil to be examined with two volumes of petroleum ether, and cooling the mixture to minus  $16^{\circ}\text{C.}$ , at the end of a few minutes the mass coagulates and the oil separates if castor oil is present, while the liquid remains homogeneous if it is pure. This phenomenon is especially curious because it will be noted that the freezing point of castor oil unmixed with petroleum ether is much lower than the majority of other oils.

#### SOLID VEGETABLE OILS.

*Cocoonut and Palm Kernel Oils.*—The production of these oils, which is continually increasing on account of their great value for the manufacture of soap during the last few years, has been made the object of several adulterations. Independently of the general, chemical, and physical characters of these oils, as well as the sulphuric saponification which I have mentioned, we can employ with good results the determination of the saturation equivalent with normal caustic soda solution.

These oils, containing a greater amount of the lower fatty acids, require, for their saturation, a larger quantity of sodium oxide. It is only necessary to determine the number of cc. of normal solution required for the saturation of five grams of the pure fatty acid to recognize these oils,—cocoonut oil 24.1, palm kernel oil 22.5, while the average of the other liquids is seventeen or eighteen cc. only. This process presents some inconveniences, especially when trying to discover small quantities of

adulteration, because it must be noted that the adulteration of these oils is only practiced within certain limits, otherwise their appearance would lead to its detection. Besides, when an oil is made from old or spoiled seeds the saturation is a little less.

Since the detection of adulterations in these oils depends on variations of a few tenths of a centimeter which might be caused by the variation of the oils themselves, or the method of operating, it is necessary to be very circumspect in the use of this truly scientific process.

With palm kernel oil this error might be greater because it is customary to balance the low saturation of the seed oils by the addition of cocoanut oil. As, for example, five grams of fatty acids from a mixture containing forty-five per cent. of palm kernel oil, forty-five per cent. cocoanut oil, and ten per cent. peanut oil, require precisely 22.5 cc. normal solution for their saturation.

*Iodine Number.*—This determination is very useful because these oils being very rich in saturated acids absorb much smaller quantities of iodine than most other oils. For example, peanut gives ninety-seven while cocoanut and palm kernel show only nine to sixteen. Unfortunately this difference of seven between the maximum and minimum throws us out of the way for small quantities of admixture, so much so that different authors fail to agree upon the average variation—some giving eight to nine only, while we are accustomed to find from thirteen to fifteen.

To resume this process, which, if it gave constant results, would be excellent, fails to give sufficiently accurate indications to detect adulteration of cocoanut oil when in small proportions. It is worse with palm kernel oil and of no value to distinguish between the two.

Continuing our investigations in another direction we have fortunately found a process which gives constant results when used upon these oils after a preliminary neutralization. We have discovered that cocoanut and palm kernel oils are entirely soluble in absolute alcohol. At a temperature of 30°-31° C. the former requires two volumes and the latter four volumes for complete solution.



It is a curious phenomenon that the smallest addition of vegetable or animal oils destroys this solubility in the same quantities of absolute alcohol. The solubility of the mixture is not proportional to its composition, but the mixture acts entirely like a distinct body.

*Mode of Procedure.*—First operation: Twenty cc. of the oil are shaken in a test tube with forty cc. of ninety-five per cent. alcohol. This indispensable preliminary treatment may give certain indications. Oil soluble in ninety-five per cent. alcohol, castor, resin oil, etc., are thus discovered, while Mowrah and Karité oils give a milky turbidity to the alcoholic stratum.

Second operation: Five cc. of the neutralized cocoanut oil are measured with a pipette into a graduated test tube, and ten cc. absolute alcohol added. The temperature is raised to  $31^{\circ}$ , the tube shaken violently for half a minute and then immersed in a water bath, kept at a temperature slightly above that of the tube. Pure cocoanut oil dissolves completely, and the solution remains clear. Any addition of another fatty matter causes precipitation. The material in solution being in a state of molecular equilibrium which is destroyed by the slightest modification.

Cocoanut oil, containing palm kernel oil, precipitates when the proportion of the mixture amounts to twenty per cent.; below this the mass remains turbid.

The verification of palm kernel oil is made in the same manner, only using twenty cc. absolute alcohol instead of ten, temperature remaining the same,  $30-31^{\circ}$ ; five cc. of palm kernel oil, containing twenty per cent. of cocoanut oil, and above, dissolves in fifteen cc. absolute alcohol. In the same proportions pure oil does not dissolve and the mixture remains turbid.

A mixture of cocoanut, palm kernel, and peanut oil in such proportions that the oil would appear pure by the indices of saturation would be easily discovered by this process.

If we work at a lower temperature the proportion of absolute alcohol must be increased. For example, at  $25-26^{\circ}$  it is necessary to double the quantity; for five cc. of cocoanut oil, twenty cc. of alcohol, and for the palm kernel nut forty cc.

The same method may be used to determine the purity of co-

coanut and palm kernel cakes by first extracting the oil by means of a solvent and then operating on it in the manner described.

This process, which I have had the honor to describe, carefully executed will allow us to determine in a few minutes adulterations of these oils which might cause bad results in soap making, which employs hundreds of millions of kilograms per annum, and in agriculture which uses the cakes for cattle food. This process was presented to the Academy of Sciences, Oct. 10, 1892, by M. L. Troost, and has been the object of a favorable report to the minister of agriculture.

Let us pass rapidly over palm oil whose principal chemical properties possess nothing in particular except its partial solubility in absolute alcohol, which is ten per cent. Also, we will pass over the Mowrah, which, as I have already mentioned, is identified by the milky white turbidity which it communicates to alcohol by shaking.

Illepe oil, whose titer is  $52.5^{\circ}$ , and cotton-seed margarine or stearine, as it is called here, whose chemical reactions are the same as the oil itself, will not long detain us.

I wish to mention, while closing the description of the solid vegetable oils, Karité oil, which comes from the French province, Soudan, which I have been especially directed to investigate by the Chamber of Commerce, of Paris, and the Chamber of the Syndicate for the manufacture of soap and candles.

It was very important for us to know how to utilize the great forest which covered the largest part of French Soudan. It is composed chiefly of the wild acacia and the Karité or butter tree. The natives collect the nuts which fall from the trees, crush the kernels in a mortar, treat the pasty mass with boiling water, and skim off the fat which comes to the surface. This fat, which is solid at the ordinary temperature, is used as an edible butter.

Without speaking about the great uses to civilization of this product, I must mention its remarkable chemical properties. The fatty acids having a titer of  $52.5^{\circ}$  C. combine with soda to produce an extremely hard soap. For candle making they would probably give better results after preliminary treatment

to remove the resinoid matters which they contain and which hinder the crystallization of the fatty acids.

The presence of these resins lower the saturation to 14.9, and like the Mowrah this oil causes turbidity by shaking with alcohol (communication of M. Milliau to the Société d'Encouragement de Paris in 1892).

SOLID ANIMAL FATS, COLORED BROWN BY A STREAM OF  
CHLORINE GAS.

*Butter.*—The analysis of this material, which has attracted so much attention during the last few years, is not so difficult as some folks imagine, but requires to be carried on by the skill of a practical and experienced analyst. The specific gravity of butter is notably lower than that of tallow and lard. It is the same with the iodine number and the freezing point of the neutral fat. The saponification and the solubility in absolute alcohol on the contrary are notably higher.

We can combine with these different characters microscopical examination, melted butters showing under the microscope a collection of small regular spheres. Adulterated butter shows on the contrary abnormal figures as well as crystals which appear brilliant in the dark field of the polarizer.

By determining the fixed and volatile fatty acids and the solubility in alcoholic toluene, a skilled analyst familiar with these processes can easily determine admixtures above ten per cent. Below this point I do not believe any adulteration would be profitable. Natural butter contains about eleven per cent. soluble and volatile fatty acids, and eighty-seven per cent. fixed fatty acids. Besides alcoholic toluene dissolves it almost entirely.

*Tallow.*—The properties of tallow are so well known that they require no description. The distinction between beef and mutton tallow is a matter of interest, and presents great difficulties from the chemical standpoint, and we can only observe differences by taking the melting and solidifying points of the neutral fat and those of the fatty acids.

*Lard.*—Lard adulterated with cotton-seed oil is easily tested with nitrate of silver.

If the lard has been altered by time or other causes, it is necessary before using this reagent upon the fatty acids to take the precaution of purifying the fat in the manner in which I have indicated at the beginning of this article. We will thus avoid the slight reduction which is produced by decomposition products.

Some authors strongly believe in the use of the iodine number, which will give good results in the cases of large admixtures, as well as for quantitative analysis of such a mixture. But it is quite illusory for the detection of a small proportion of cotton-seed oil, for we must consider that the iodine number of pure lard varies within considerable limits, and it would be possible to correct for the high iodine number of cotton-seed oil by the addition of tallow, which will lower it appreciably. In such a mixture the action of nitrate of silver on the fatty acids allows us to discover adulteration even below five per cent. Tallow is detected by observing the crystallization of the fat from ethereal solution under the microscope.

The following oils, which frequently are used for the adulteration of agricultural fatty materials, are easily detected:

*Fish Oil.*—By its iodine number, its solubility in absolute alcohol, the presence of cholesterine, and finally the brown coloration by chlorine and red by caustic soda and phosphoric acid.

*Resins.*—By their density, their saturation, their solubility in absolute alcohol, and the deviation of the plane of polarization. Besides, it is easy to isolate them because the majority of compounds which they form with metallic salts are soluble in ether, while those of the fatty acids are insoluble.

*Resin Oils.*—By their property of not saponifying with caustic soda as well as by their insolubility in glacial acetic acid, and the characteristic purple coloration which they give with fuming stannic chloride.

*Oleine Oil of Commerce.*—By its solubility in alcohol and by its specific gravity.

Finally, *the mineral oils*, by their iodine numbers, their indifference to the action of caustic soda, and their insolubility in absolute alcohol at 15° C.

The processes which I have just enumerated are applicable

indiscriminately to fatty matters both edible and industrial, for the recognition of their purity with an approximation sufficient for the majority of cases.

The results obtained will be more conclusive if they are compared with those from products of the same origin and known purity.

Although the majority of the processes which I have just indicated were devised and perfected in my laboratory and have been adopted by several governments, I have not, however, the presumption to feel that we have definitely finished this question, but consider on the contrary that in the vast unexplored region of the fatty series we have only taken a few steps. But I feel at the same time that we are now in the possession of sensitive and scientific methods which permit us to detect mixtures, the determination of which has appeared impossible up to the last few years.

The mission with which I have been charged by the French and Tunisian governments at the demands of commerce and industry shows you to what extent these countries are desirous of facilitating the exportation of pure and satisfactory products. France furnishes the best growth of virgin olive oil from Aix en Provence and Nice. On its side Tunis furnishes as well, but at a less price, olive oils of excellent quality which we can certify without analysis, because the government imposes such heavy export and import duties upon seed and seed oils that it would be impossible to practice the smallest amount of sophistication.

Often people who deal in olive oils make the remark that pure oil is too strong and it is improved in flavor by a mixture with a seed oil. Without discussing this inexact statement I believe that it would be preferable in every instance for the dealer to buy pure olive oil and to make his own mixtures. He would thus profit by the difference in price, which averages about sixty francs per 100 kilograms.

## THE TORSION VISCOSIMETER.<sup>1</sup>

BY O. S. DOOLITTLE.

**T**HE viscosity of an oil is recognized to-day by both the producer and consumer as the most valuable measure of its lubricating power, and yet we find no uniformity whatever in the manner of determining this essential property.

There are numerous viscosimeters in use, but no one of them has commended itself to the trade sufficiently to be adopted as a standard.

Many of them have their good features, but all have objections which have prevented any one from being accepted as standard and universally used.

The essentials of a good viscosimeter are :

(1) Accuracy, including both the ability to duplicate results obtained with an oil on the same instrument, and also on different instruments of the same make.

(2) Ease and rapidity of cleaning and manipulating, and the reducing of personal error to a minimum.

(3) Adaptability of a single instrument to all kinds of oil at all desirable temperatures.

The great majority of viscosimeters are built on the principle of allowing the oil to flow through an orifice and counting the number of seconds required for a certain quantity to flow out. Instruments constructed on this plan cannot be made to conform satisfactorily to all the above requirements.

As a rule it takes more time to clean and get the viscosimeters of this class ready for a test, than for the test itself.

If the instrument is made with great care good duplicate results can be obtained with a perfectly clean oil,



DOOLITTLE'S TORSION VISCOSIMETER.

<sup>1</sup> *Drugs, Oils and Paints*, June, 1893.

but if by any chance a slight particle of dirt gets into the oil the orifice is liable to become obstructed and the results vitiated.

At the same time these results are but comparative, and poorly comparative at the best, as the head of oil is constantly changing from the moment the flow begins, and the rapidity of the flow must necessarily depend more or less upon the specific gravity of the oil.

That the personal error is a large one will hardly be disputed by any who have worked with these instruments. Again, you will find as a rule several different viscosimeters with varying orifices required for the different oils, a small hole being the best for light oils and a large one for the heavy products.

Thus we have, no regular scale of viscosities ranging upward from some recognized zero point, which by the way water furnishes admirably.

This is a most unfortunate state of affairs, as it deprives us of a standard by which the value of all oils could be readily recognized and intelligently understood. When we speak of a temperature of  $212^{\circ}$  it is well understood because the Fahrenheit thermometer is recognized as a standard in this country, but when we refer to a viscosity of 125 seconds it has no meaning whatever unless it is accompanied by the name of the instrument on which it was obtained, and oftentimes the name of the observer as well, thus necessitating the carrying in mind of the ratio of numerous instruments to each other, a very perplexing and unsatisfactory task.

Having experimented with a number of these viscosimeters in the laboratory of the Philadelphia and Reading railroad, we found them so very unsatisfactory where rapid and accurate work is required that we abandoned them all and designed an instrument on an old principle which has been used in measuring almost everything from a delicate electrical current to the quantity of cream in milk, an operation at times requiring a still more sensitive instrument, *i. e.*, that of the torsion balance.

The principle has not failed us in this case, and in the torsion viscosimeter we have an instrument which, during the year we have had it in daily use, has proved itself reliable, accurate, and satisfactory in every way.

It is very easy to clean and manipulate, is adapted to oils of all ranges of viscosity from kerosene up, and reduces the personal error to a minimum.

A glance at the cut will show how the principle has been applied.

A steel wire is suspended from a firm support and fastened to a stem which passes through a graduated horizontal disk, thus allowing us to measure accurately the torsion of the wire. The disk is adjusted so that the index point reads exactly zero, thus showing that there is no torsion in the wire.

A cylinder two inches long by one and a half inches in diameter, having a slender stem by which to suspend it, is then immersed in the oil and fastened by a thumb-screw on the lower part of the stem to the disk. The oil is surrounded by a bath of water or paraffine wax according to the temperature at which it is desired to take the viscosity. This temperature being obtained, while the disk is resting on its supports, the wire is twisted  $360^\circ$  by means of the knob at the top. The disk being released, the cylinder rotates in the oil by virtue of the torsion of the wire.

The action now observed is identical with that of the pendulum.

If there was no resistance to be overcome, the disk would revolve back to zero, and the momentum thus acquired would carry it to  $360^\circ$  in the opposite direction. What we find is that the resistance of the oil to the rotation of the cylinder causes the revolution to fall short of  $360^\circ$ , and that the greater the viscosity of the oil the greater will be the resistance and hence the retardation. We find this retardation to be a very delicate measure of the viscosity of an oil.

There are a number of ways in which this viscosity may be expressed, but the simplest we have found to be directly in the number of degrees of retardation between the first and second complete arcs covered by our pendulum. For example, suppose we twist the wire  $360^\circ$  and release the disk so that rotation begins. In order to obtain an absolute reading to start from, which shall be independent of any slight error in adjustment, we ignore the fact that we have started from  $360^\circ$ , and



take as our first reading the end of the first swing. Suppose our readings are as follows:

Right, 350; left, 338; right, 328, and keeping in mind the vibrations of the simple pendulum we will see at once that we have read two complete arcs whose difference is  $22^\circ$  computed as follows:

$$\begin{array}{r} \text{1st arc, Right } 350^\circ + \text{Left } 338^\circ = 688^\circ \\ \text{2d arc, Left } 338^\circ + \text{Right } 328^\circ = 666^\circ \\ \hline 22^\circ \text{ retardation} \end{array}$$

In order to secure freedom from error we take two tests—one by rotating the wire to the right, and the second to the left. If the instrument is in exact adjustment these two results will be the same, but if it is slightly out, the mean of the two readings will be the correct reading.

It will also be noticed that if the exact retardation due to the oil alone is to be obtained we must subtract the factor for the resistance due to the air and the wire itself. These are readily obtained by allowing the cylinder to rotate in the air and determining the retardation exactly as we have done above. This factor remains constant for each instrument and is simply deducted from all results obtained.

The torsion viscosimeter is free from many of the objections noticed in other instruments, and has given entire satisfaction during the period it has been in use. It is independent of the gravity of the oil and of any reasonable amount of dirt which may get into it. It is applicable to all grades of oil regardless of their character or fluidity. The viscosity of an oil can be taken at any temperature as many times as may be desired without any inconvenience from being obliged to handle the hot oil.

This I think is an important point, as the practice in common use of determining the viscosity of a cylinder stock at  $212^\circ$  Fahrenheit does not tell us what we want to know. We should know the viscosity of an oil at the temperature at which it is to be used, which, in the case of cylinder stock, is in the neighborhood of  $350^\circ$ . I have repeatedly found oils tested at  $212^\circ$  simply reversing their comparative values when heated to  $350^\circ$ .

We need a viscosimeter with which the viscosity can readily

be determined at a high temperature with a minimum amount of trouble. By means of a paraffine bath for our oil we have no trouble whatever in doing this with the torsion viscosimeter.

When one oil has been tested sufficiently the cylinder can be taken out in a moment, wiped off, and is then ready for another oil.

The necessity of a standard instrument which shall be recognized by the trade as such cannot be too forcibly emphasized, as the present state of affairs is most annoying to both producer and consumer, leading as it so often does to misunderstanding and financial loss.

The torsion viscosimeter is the standard instrument of the Philadelphia and Reading railroad, but this simply means that it is the best we know of at present. We are, however, always open to conviction, and if any better method of determining the viscosity of an oil is invented we will be very glad to adopt it.

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#### FIFTH GENERAL MEETING.

THE following resolution was adopted by the Council of the American Chemical Society, June 7, 1893 :

*Resolved*, That the General Meeting of the American Chemical Society for the summer of 1893 be held in Chicago at such date as may be determined by the committee appointed by the society to co-operate with the World's Fair Auxiliary of the Columbian Exposition in arranging for an International Congress of Chemists.

In accordance with the terms of this resolution the committee to co-operate with the World's Fair Auxiliary have determined that the Fifth General Meeting of the Society shall be held during a period beginning August 21, 1893, in conjunction with the World's Congress of Chemists to be held under the auspices of the World's Fair Auxiliary and the American Chemical Society.

The committee desire to call to the attention of the members of the society and of American chemists generally, the fact that in view of the large number of eminent chemists, home and foreign, who have already signified an intention to attend the World's Congress of Chemists, and the valuable character of

the papers that will be presented, this meeting will doubtless be the most important gathering ever held by chemists in the United States. The time and place are therefore particularly auspicious, and the promise of a most successful and enjoyable occasion very great. The meetings will be open to all chemists in good standing, and in order that a program of proceedings may be arranged in advance, it is earnestly requested that those who desire to offer papers will forward titles thereof as early as August 1, to Prof. Wm. McMurtrie, 106 Wall street, New York City, care of New York Tartar Co.

It is also the hope of the committee that in view of the important part taken by the American Chemical Society in calling the World's Congress of Chemists, the society will be represented by a large number of its members in this meeting. This is due to the foreign chemists who have accepted the invitations extended by the society.

In matters of transportation to, and quarters in, Chicago, members of the society will have all the advantages provided for those who will attend the World's Congress of Chemists. Those desiring information with this regard may obtain it by addressing Prof. John H. Long, No. 2421 Dearborn avenue, Chicago, Ill.

It is requested that as soon as possible after their arrival in Chicago, members will report at the Congress Headquarters in the Art Institute Building, Lake Front and Adams street, and register their names and Chicago addresses so that they may receive without delay such notices and information as the committees may have to distribute at that time.

WM. McMURTRIE,  
C. F. CHANDLER,  
A. B. PRESCOTT,  
C. E. MUNROE,  
H. W. WILEY,

Committee to Co-operate with the World's Fair Auxiliary.

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, etc.*—James B. Montgomery has a new form of ore concentrator (495,003). Orrin B. Peck adds one more to his list of patents on a centrifugal ore separator (495,681), and M. W. Iles covers his process of and apparatus for the extraction of matte from slag by numbers 494,570 and 494,571. A. L. Engelbach and S. E. Bretherton have an apparatus for reducing and smelting sulphide ores (496,250). Charles M. Allen takes out three related patents: 496,032 treats of his process of smelting ores and refining metals, which is conducted in a converter (496,033), which has a patent tuyere (496,034). The ores are fed into this converter and the blast is passed through the molten metal for a time, then checked by plugging the tuyeres to permit slag, matte, and metal to separate in the converter at different heights, and enough molten metal is retained each time to ignite the next charge. Thomas A. Edison has a roller for crushing ores (498,385). N. L. Raber (497,603) and A. B. Kittson (497,669) have each an amalgamator, and Uriah Cummings patents his ore crusher (498,424). C. B. Walker has a new form of ore concentrator (497,843), and Charles G. Brown a patent ore tank for leaching (497,856). Orrin B. Peck protects his centrifugal ore separator by 497,204, while F. H. Wheelan (498,597), W. P. Miller (497,474), Charles G. Buchanan (497,117), and Albert M. Bair (496,391) have each a separator. William Stubblebine's metallurgical furnace (498,089) and M. Mannaberg's steel-smelting furnace (498,670) are recent issues, as well as Joseph McClelland's tuyere (498,565). An apparatus for removing matte from slag is the joint invention of Thomas Drohan and Thomas Pearce (496,823). John W. Marshall is the patentee of an ore-stamping mill (493,384) and of an ore stamp (493,385). Charles J. Fauvel has a new furnace for the treatment of refractory ores (493,076). C. W. Beehler is the inventor of a hydrothermal mining process (497,513), which consists in filling a closed casing with a liquid body, inserting in bore hole, and heating by electric resistance coil, so that the expansive force of the liquid may be exerted within the drill hole.

*Lead.*—"Sublimed lead pigments" are prepared by E. O. Bartlett by driving off lead fumes from lead-bearing material in suitable furnaces, carrying the fumes through flues at a red heat, and separating the purified fumes by screening from the gaseous products (496,038). Two more patent processes for the manufacture of white lead. 496,109, A. B. Browne, patentee, consists in placing lead in a solution of a nitrate of an alkaline base; the current is then passed and the alkaline hydrate formed at one pole precipitates the lead which has been dissolved, and the resultant lead hydrate is dried in an atmosphere of carbon dioxide. 495,490 is the invention of Andrew Honman and Victor Vulliez. Lead sulphate is dissolved in a solution of caustic soda or potash or ammonium acetate, heated, and precipitated with an alkaline carbonate and dried.

*Fertilizers.*—Ludwig Rissmüller manufactures superphosphates from kettle residues of glue factories by mixing residues with warm sulphuric acid ( $50^{\circ}$  B.) and heating to  $200^{\circ}$  F. After the nitrogenous matters are dissolved by the acid, the gypsum is precipitated and the fat rises to the surface, the separated solution is treated with phosphate of lime to take up all the sulphuric acid (494,939). 494,940 is a similar process, applied to animal carcasses, etc. Omar T. Joslin treats tank water with sulphuric acid, adds five to thirteen per cent. of a concentrated solution of waste fullers' earth dissolved in sulphuric acid, and dries the product at  $300^{\circ}$ – $350^{\circ}$  F. (495,042); and 495,043 is also his patent for manufacturing fertilizer from tank water in which acid phosphate of calcium in combination with fullers' earth is used, instead of the latter alone. Philip C. Hoffman treats pulverized phosphates of the "Florida phosphate" class with sulphuric acid, heats, and maintains the temperature above the normal temperature occasioned by chemical action, which is usually  $50^{\circ}$  C., but yet below that at which pyrophosphates are formed (496,687). Robert Reiman chemically dissolves natural bone or bone meal into its constituents, precipitating these elements, filters and washes and afterwards mixes with albumen, aluminum sulphate, and cellulose in solution, dries partly, then subjects to a high temperature and powerful pressure simultaneously, thus manufacturing artificial bone (494,891).

*Gold and Silver.*—Wm. Birkin subjects ores to the action of potassium cyanide, potassium ferricyanide, and hydrogen peroxide to extract the precious metals (494,054). For the lixiviation of gold and silver ores Samuel R. Whitall first mixes them with either caustic soda or potash, then treats with a solution of potassium cyanide and sodium hyposulphite and precipitates the precious metals by electrolysis (495,715). Fred. Webb has an apparatus for extracting precious metals from their ores (495,385), and John F. Wiswell treats ores as follows: Mercury is submerged in a solution of common salt which is electrolyzed. The calomel formed is dissolved in aqua regia, forming mercuric chloride, while the undecomposed salt solution is further electrolyzed, forming sodium hypochlorite. The ores are then treated simultaneously with both solution of the hypochlorite and mercuric chloride, and the dissolved metals are precipitated by adding bright iron fragments (495,212). F. W. Cleghorn separates precious metals from their ores by filtering through the ores a solution of sulphuric acid and sodium chloride, placing metallic iron in the filtrate and passing the current (497,014), while Henry Parkes uses one of two methods to accomplish the same end, treating the ores with potassium cyanide in the presence of oxygen under pressure (496,950), or treating with chlorine and then agitating with oxygen under pressure (496,951). Jabez Turton proposes to separate metals from ores by treating the ore or mineral to the action of a nitrate of an alkali metal, sodium chloride, and sulphuric acid, separating the earthy matters and precipitating the metals (494,044).

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

BY THOS. B. STILLMAN, PH.D.

THE enlarged consumption of Portland cement in this country during the past few years has caused the subject of its chemical and physical properties to receive increased consideration. Not only has the consumer been directly interested, that the cements used should stand specified tests, but the attention of the manufacturer has been drawn in the same direction, resulting in improvements in methods of production.

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SCHEME FOR THE ANALYSIS OF PORTLAND CEMENT. BY THOS. B. MILLMAN.

Weigh out 2 gms. of the finely powdered and dried material, transfer to a 6-inch porcelain capsule, add 5 cc. HCl, 5 cc. H<sub>2</sub>O and evaporate to dryness and 25 cc. HCl, 100 cc. H<sub>2</sub>O, boil and filter into a 1 liter flask; wash well, make solution up to contain 1 mark and thoroughly mix.

(2) *Solution 1*.—Take 1 sample of 100 cc., transfer to a 300 cc. beaker, make alkaline with NH<sub>4</sub>OH, warm, filter, and wash.

<i>Residue</i> , SiO <sub>2</sub> .	<i>Solution</i> .— Make alkali- Dry, ignite and weigh as SiO <sub>2</sub> .	<i>Residue</i> , Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , and weigh as Fe <sub>2</sub> O <sub>3</sub> . Subtract this weight from the weight in Al <sub>2</sub> O <sub>3</sub> .	<i>Solution</i> , containing Al <sub>2</sub> O <sub>3</sub> . If it is desired to weigh Fe <sub>2</sub> O <sub>3</sub> , this solution with HCl, then make faintly al- kaline with NH <sub>4</sub> OH; boil, filter, wash well. The pre- cipitate is dried, ig- nited and weighed as Al <sub>2</sub> O <sub>3</sub> .
(1) <i>Residue</i> .—Dry, ig- nite, fuse in platinum crucible with Na <sub>2</sub> CO <sub>3</sub> ; cool, dissolve in water, acidify with HCl, evapo- rate to dryness in 4-inch porcelain capsule; take up with HCl and water; boil, filter and wash.	(3) <i>Residue</i> , Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> . Dry, ignite and weigh as such. Then fuse in silver dish with KHO. Treat with water, boil, and filter.	(4) <i>Solution</i> .—Add ammonium oxalate in slight excess, set aside 4 hours, filter, wash with water containing ½ its bulk of ammonium hydrate.	(5) <i>Residue</i> is CaC <sub>2</sub> O <sub>4</sub> . Dry, ignite over blast- lamp to constant weight. Weigh as CaO.
(6) <i>Residue</i> is MgO. Dry, ignite and weigh as MgO.	(7) <i>Residue</i> is MgO. Dry, ignite and weigh as MgO.	(8) <i>Solution</i> .—Transfer to a weighed platinum capsule, add a few drops of H <sub>2</sub> SO <sub>4</sub> and evapo- rate to dryness; ignite to constant weight. This weight represents Na <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub> . Dis- solve in 50 cc. of H <sub>2</sub> O, mix well and divide into 2 portions of 25 cc. each.	(9) <i>Solution</i> .—Add a few drops of HCl, then make alkaline with NH <sub>4</sub> OH, and precipitate the Mg with solution of Na <sub>2</sub> HPO <sub>4</sub> . Set aside 3 hours, filter, wash with ammoniated water, dry, ignite and weigh as Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> , and calculate to (MgSO <sub>4</sub> ). This weight, multiplied by 2, is subtracted from weight of total sulphates in (8). Calculate MgSO <sub>4</sub> to MgO.
<p><i>1st Portion</i>.—Add solution of PtCl<sub>4</sub> in slight excess, a few drops of HCl and evaporate to dryness on the water-bath. Determine weight of K<sub>2</sub>PtCl<sub>6</sub> on tared fil- ters and calculate to K<sub>2</sub>SO<sub>4</sub>. Multiply this by 2 and subtract weight from total sulphates. The weights of K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> subtracted from total sulphates gives the remainder as Na<sub>2</sub>SO<sub>4</sub>. Calculate K<sub>2</sub>SO<sub>4</sub> to K<sub>2</sub>O. Calculate</p>			
<p><i>2d Portion</i>.—Add solution of PtCl<sub>4</sub> in slight excess, a few drops of HCl and evaporate to dryness on the water-bath. Determine weight of K<sub>2</sub>PtCl<sub>6</sub> on tared fil- ters and calculate to K<sub>2</sub>SO<sub>4</sub>. Multiply this by 2 and subtract weight from total sulphates. The weights of K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> subtracted from total sulphates gives the remainder as Na<sub>2</sub>SO<sub>4</sub>. Calculate K<sub>2</sub>SO<sub>4</sub> to K<sub>2</sub>O. Calculate</p>			
<p>Crucible + MgO = 10.725 Gms. MgO = 0.004 MgO from (8) = 0.008 0.008 x 0.5 x 100 = 0.4 0.008 x 0.5 x 100 = 0.4 MgO = 1.225</p>			
<p>Crucible + BaSO<sub>4</sub> = 10.731 BaSO<sub>4</sub> = 0.006 0.006 x 0.5 x 100 = 0.3 0.006 x 0.5 x 100 = 0.3 BaSO<sub>4</sub> = 0.677</p>			
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## RÉSUMÉ.

	Per cent.
SiO <sub>2</sub> .....	24.20
Al <sub>2</sub> O <sub>3</sub> .....	6.22
Fe <sub>2</sub> O <sub>3</sub> .....	3.00
CaO.....	62.67
MgO.....	1.22
K <sub>2</sub> O.....	1.10
Na <sub>2</sub> O.....	0.86
SO <sub>3</sub> .....	0.67
Total.....	99.94

The following well known brands of Portland cements were analyzed in my laboratory by above method.

	Burham's.	Dyckerhoff's.	Saylor's.
SiO <sub>2</sub> .....	21.70 per cent.	19.05 per cent.	21.25 per cent.
Al <sub>2</sub> O <sub>3</sub> .....	6.82 "	7.90 "	4.21 "
Fe <sub>2</sub> O <sub>3</sub> .....	2.37 "	5.38 "	8.25 "
CaO.....	62.26 "	63.62 "	61.25 "
MgO.....	1.48 "	1.87 "	1.50 "
K <sub>2</sub> O.....	1.84 "	0.88 "	1.01 "
Na <sub>2</sub> O.....	0.98 "	0.36 "	0.99 "
SO <sub>3</sub> .....	1.20 "	0.94 "	1.38 "
CO <sub>2</sub> .....	1.30 "	....	....
	99.95 "	100.00 "	99.84 "

In some cements quartz is a constituent in amounts varying from 0.5 to 6 per cent. It can be separated from combined silica by the method of Fresenius (*Quant. Chem. Anal.*, p. 259).

Where carbonic acid has been indicated by the qualitative analysis the quantitative analysis should be made upon at least eight grams of the cement.

The carbonic acid rarely reaches one per cent., and while it is generally absent in well-burned cements, it is by no means an uncommon constituent to the amount of 0.15–0.30 per cent., as the following table of analyses of German cements will show<sup>1</sup>:

	1	2	3	4	5	6	7	8
CaO.....	61.99	62.89	63.71	63.27	65.59	59.96	64.51	60.81
SiO <sub>2</sub> .....	23.69	22.80	25.37	19.80	22.85	23.70	22.38	22.63
Fe <sub>2</sub> O <sub>3</sub> .....	2.71	3.40	3.14	3.22	2.76	3.15	2.24	2.42
Al <sub>2</sub> O <sub>3</sub> .....	8.29	7.70	4.31	6.73	5.51	8.20	9.45	7.06
MgO.....	0.47	1.20	1.25	2.02	1.24	1.00	....	2.89
Alkalies...	0.95	1.30	0.84	1.48	0.92	1.05	....	2.83
SO <sub>3</sub> .....	0.69	0.71	0.87	1.08	1.60	0.88	1.44	0.47
CO <sub>2</sub> .....	0.27	....	....	0.23	....	0.26	....	0.33
Insoluble..	0.44	....	....	1.38	....	0.80	....	....

<sup>1</sup> *Der Portland-Cement und seine Anwendungen im Bauwesen*, Berlin, 1892, p. 18.

## THE MECHANICAL TESTING.

The method recommended for use in this country by the American Society of Civil Engineers is as follows:

- (1) Determination of fineness.
- (2) Liability to checking or cracking.
- (3) Tensile strength.

*Fineness.*—Tests should be made upon cements that have passed through a No. 100 sieve (10,000 meshes to the square inch), made of No. 40 wire, Stubb's wire gauge. The finer the cement the more sand it will unite with and the greater its value.

*Liability to Checking or Cracking.*—Make two cakes of neat cement two or three inches in diameter, about one-half inch thick, with thin edges. Note the time in minutes that these cakes, when mixed with mortar to the consistency of a stiff, plastic mortar, take to set hard enough to stand the wire test recommended by General Gillmore, one-twelfth inch diameter wire loaded with one-fourth pound, and one twenty-fourth inch diameter wire loaded with one pound.

One of these cakes, when hard enough, should be put in water and examined from day to day to see if it becomes contorted or if cracks show themselves at the edges. Such contortions or cracks indicating that the cement is unfit for use at that time. In some cases the tendency to crack, if caused by too much lime, will disappear with age. The remaining cake should be kept in the air and its color observed, which, for a good cement, should be uniform throughout.

*Tensile Strength.*—One part of the cement mixed with three parts of sand for the seven days and upward test, in addition to the trials of the neat cement. The proportions of cement, sand, and water should be carefully determined by weight, the sand and cement mixed dry, and all the water added at once. The mixing must be rapid and thorough, and the mortar, which should be stiff and plastic, should be firmly pressed into the molds with the trowel without ramming and struck off level, the molds in each instance, while being charged and manipulated, to be laid directly on glass, slate, or other non-absorbent material. The molding must be completed before incipient

setting begins. As soon as the briquettes are hard enough to bear it, they should be taken from the molds and kept covered with a damp cloth until they are immersed. For the sake of uniformity, the briquettes, both of neat cement and those containing sand, should be immersed in water at the end of twenty-four hours, except in the case of one day tests. Ordinary clean water having a temperature between 60° F. and 70° F. should be used for the water of mixture and immersion of sample. The proportion of water required is approximately as follows:

For briquettes of neat cement, about twenty-five per cent.

For briquettes of one part cement, one part sand, about fifteen per cent. of total weight of cement and sand.

For briquettes one part cement, three parts sand, about twelve per cent. of total weight of cement and sand.

The object is to produce the plasticity of rather stiff plasterer's cement.

An average of five briquettes may be made for each test, only those breaking at the smallest section to be taken. The briquettes should always be put in the testing machine and broken immediately after being taken out of the water, and the temperature of the briquettes and of the testing room should be constant between 60° F. and 70° F.

The following table shows the average minimum and maximum tensile strength per square inch which some good cements have attained. Within the limits given the value of a cement varies closely with the tensile strength when tested with the full dose of sand.

AMERICAN AND FOREIGN PORTLAND CEMENTS.—NEAT.

1 Day (1 hour, or until set, in air, the rest of the 24 hours in water) ..	.....from 100 to 140 lbs. per square inch
1 Week (1 day in air, 6 days in water) ..	.....from 250 to 550 lbs. per square inch
1 Month, 28 days (1 day in air, 27 days in water) ..	.....from 350 to 700 lbs. per square inch
1 Year (1 day in air, the remainder in water) ..	.....from 450 to 800 lbs. per square inch

AMERICAN AND FOREIGN PORTLAND CEMENTS.—1 PART OF CEMENT TO  
3 PARTS OF SAND.

1 Week (1 day in air, 6 days in water) ..	.....from 80 to 125 lbs. per square inch
1 Month, 28 days (1 day in air, 27 days in water) ..	.....from 100 to 200 lbs. per square inch

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While the Portland cement manufacture here is yet in its infancy, with a history of practically less than ten years, its product for 1891 reached a total of 450,000 barrels out of 3,500,000 barrels consumed in this country during that year. This ratio between home production and importation should be radically changed in the near future, since the product for 1892 was over 600,000 barrels. A number of causes have prevented the use of American Portland cements in the home market, one of the chief being that the imported German cements always gave higher physical tests when made by the German methods of testing than the American cements under the American system of testing. There are a number of American Port-

*Directions for Testing Portland Cement According to the Official German Rules*.—The quality of a mortar made with cement depends not only on the strength of the cement itself, but also on the degree of sub-division of the same. It is therefore necessary to make the tests both with neat cement and with a mixture of the same with "standard sand." This latter as used at the Royal Testing Station at Berlin, is produced by washing and drying quartz sand, which must be clean as possible, and afterwards be sifted through a sieve of sixty meshes per square centimeter (387 meshes per square inch), by which process the coarsest particles are separated. The sand is again sifted through a sieve having 120 meshes to the square centimeter (774 meshes per square inch). The residue remaining in this sieve is the standard sand for experiments, the coarsest and finest particles having been eliminated. It is absolutely necessary in order to obtain uniform results to use only the "standard sand," as the size of the grain has a material influence on the results of the testing. The sand must be clean and dry, and all earthy and other substances previously removed by washing.

*Preparation of Briquettes of Neat Portland Cement*.—Upon a slab of metal or marble are laid five sheets of filtering paper, which have been previously saturated with water, and upon these are placed five brass molds (Fig. 3) thoroughly clean and moistened with water. One thousand grams of cement and 250 grams of water must be thoroughly mixed, well worked up, and when the resulting mass has been rendered perfectly homogeneous, it is poured into the molds. The latter must be gently tapped by means of a wooden hammer with equal force on both sides during ten to fifteen minutes to insure the escape of confined globules of air. The molds must be carefully filled up until the mass becomes plastic, the superfluous mortar is then struck off, and the mold carefully withdrawn. The samples, after remaining twenty-four hours exposed to the air, at a temperature of about 60° F., must be immersed in water having the same temperature, and care must be taken that they remain covered with water until the



FIG. 3.

<sup>1</sup> *Portland Cement*, by Gustav Grawitz.

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is is derived, with modifications, the "Reid and Bailey" machine in use in England, and the "Fairbanks" previously escribed.

[TO BE CONTINUED.]

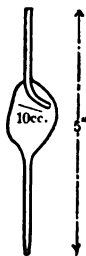
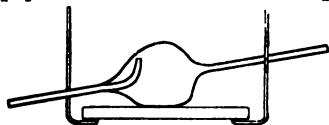
## A NEW WEIGHING APPARATUS.

BY DR. H. SCHWEITZER.

Read before the New York Section May 29, 1893.

THE weighing of liquids for analytical purposes has always been very tedious, and many forms of apparatus have been devised for facilitating this operation. But all of them had disadvantages. The distinguishing feature of our "Weighing Pipette," which was constructed with the help of our assistant, Mr. E. Lungwitz, is that it consists of a single piece without any cock or other complicated parts.

The weighing pipette presents the general appearance of a bulb pipette. Where the suction tube joins the bulb there is a short capillary tube which projects towards the wall of the bulb, the opposite wall being flattened to furnish a firm rest for the pipette on the scale.



large or small apertures of the delivery tube, according to the physical properties of the substance to be weighed. For light liquids, acids, and oils we use small apertures; for milk, syrups, heavy oils, and fats we take pipettes with large apertures.

By capillarity and suction the liquid runs back into the delivery tube without any losses. For example, we weighed a quantity of fuming sulphuric acid in a pipette with small aperture, and after half

an hour no change in the weight of the pipette was perceptible. A short delivery tube cannot be used as there is danger of the liquids running back on the outside of the tube, thereby dripping on the scales.

The pipettes can be warmed directly in the flame without danger of breaking them, in case the weighed substance solidifies in the bulb (lard, etc.).

On account of the small surface of the bulb in the little pipettes, the error in weighing slightly warmed liquids can be neglected for all practical purposes.

The inside capillary tube must be turned up as much as possible to gain space. The capillary must have a very small aperture to allow dropping and prevent liquid from entering the suction tube. The apparatus can be easily cleaned by drawing benzene or hot soda solution, etc., through it, then alcohol and ether, and drying it in a current of air.

The weighing pipette is made in different sizes with bulbs from five cc. to 100 cc., etc., etc., and is sold by E. Greiner, 146 and 148 William street, New York City.

LABORATORY OF BREYER & SCHWEITZER,  
159 FRONT ST., NEW YORK CITY.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S.  
DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 7.]

#### NOTE ON THE USE OF EOSIN FOR COLORING TOMATOES.

BY K. P. McELROY AND W. D. BIGELOW.

Received June 22.

SOME time since, in accordance with the instructions of Dr. Wiley, a qualitative examination was made of a sample of tomato color made by a Cincinnati firm and sent to the Department of Agriculture by Mr. H. E. Taylor, of Brooklyn.

The sample was in a small bottle bearing the label, "tomato color." It consisted of a thin red liquid, showing a strong fluorescence when diluted. Treated with hydrochloric acid a flocky orange precipitate was obtained and the liquid after filtration showed no color, even when made alkaline. The precipitate was freely soluble in alkalies with which it reproduced a red liquid resembling the original. It was also freely soluble in ether, giving a pale yellow solution. A portion of the sample was mixed with lime, evaporated to dryness, and burnt till white. A water solution of the resulting mixture of ash and

#### USE OF EOSIN FOR COLORING TOMATOES.

After acidifying with nitric acid, gave a heavy precipitate with silver nitrate. Another portion of the solution treated with bleaching powder and hydrochloric acid liberated a substance which was taken up by chloroform, imparting to it a strong yellow color. A portion of the original sample was reduced with sodium amalgam and to the resulting nearly colorless liquid a drop or two of dilute permanganate solution added. A liquid having a deep green fluorescence resulted. The fluorescence was so strong that the liquid was nearly opaque. In view of the reactions cited, the substance under examination was pronounced to be an aqueous solution of brom-eosin (tetra-bromfluorescein).

Eosin is one of the most extensively used of the so-called anilin colors. The statement has been made that it is sometimes employed in coloring candy, and more rarely, other articles of food. Its use for coloring tomatoes, however, has never been published to our knowledge. It is well adapted for this purpose inasmuch as in a very dilute state it possesses a yellow color not unlike that of the liquor which surrounds canned tomatoes. Addition of a single drop of the solution examined to the liquid contents of a can of tomatoes was found to hardly change the color at all, but to cause a marked change for the better in appearance.

At the suggestion of Dr. Wiley an effort was made to work out a method by which brom-eosin could be discovered when added to canned tomatoes. The readiest foundation for such a method appeared to be the fact that eosin can be readily abstracted from acidified aqueous solutions by ether, and that from this ether solution it in turn can be withdrawn by dilute alkali. The solution so obtained has a characteristic fluorescence.

A large tomato was taken, mashed, and water added. The mixture was divided into two parts and to one a drop of the tomato color added. Both portions were then placed in dishes on the water bath and heated for three hours, replacing the evaporated water from time to time. At the expiration of this time the liquid part was strained off from each portion through cotton bags. The volumes obtained in each case measure

about 150 cc. They were acidified with hydrochloric acid, placed in separatory funnels, and shaken with ether. The aqueous portion of the liquid was then drawn off and the ethereal solution washed with water. After separating from this wash water, twenty cc. of dilute solution of caustic soda were placed in each funnel and the shaking repeated. The alkaline liquid in one funnel then showed a strong yellow-green fluorescence. The color was almost exactly as intense as that produced in a similar amount of the dilute alkali by a drop of the tomato color. This was the quantity used. On once more shaking the ether remaining in the separatory funnel with alkali an aqueous solution was obtained showing a barely perceptible fluorescence. From this it was evident that the first portion of alkali had extracted practically all of the coloring matter. From the other portion of tomato, the one to which no coloring matter had been added, the alkaline liquid obtained had a slight yellow color, but showed no fluorescence.

A can of tomatoes was next procured, opened, the contents strained in a bag, and the resulting liquid divided into two parts. To one portion a drop of the eosin solution was added. Both portions were then acidulated and extracted with ether. The ether extract in both cases assumed a light yellow color. The ethereal solutions were washed with water several times and then shaken with dilute alkali. Both alkaline solutions were dark colored. Neither showed fluorescence. The ether retained some color. This, of course, was not due to eosin, which, as was just shown, is quantitatively extracted from ethereal solution by alkali. The alkaline liquids were acidified and once more extracted, using fresh ether. Nearly all the coloring matter in the acid liquid was extracted by the ether. After washing the ethereal liquids with water several times they were shaken with more alkali. The resulting solution in one case showed a faint and badly-defined fluorescence. The color of the liquid was too dark, however, to permit any certain recognition of the phenomenon. The ether was not wholly decolorized. It was thrown away, and the two aqueous solutions acidified and extracted with fresh ether. The new ethereal solutions after washing with water gave with alkalies a light

colored solution, which in one case was unmistakably fluorescent. In the other sample no fluorescence whatever was perceptible. It was therefore evident that the presence of eosin could be recognized with certainty in the presence of the natural coloring matter of the tomato even when existing in but small quantity.

Other experiments were made in which larger quantities of the tomato color were used—two, three, and four drops to 300 cc. of tomato juice. In every case recognition was positive. As a rule one or two extractions were sufficient to allow the fluorescence of the eosin to be easily recognized. Trials were made of the fluorescein reaction proposed by Baeyer<sup>1</sup> for the recognition of eosin to see if it offered any advantage, but such was not found to be the case. The test for brom-eosin, of which the sample under examination consisted, is sufficiently delicate and characteristic to render further complication unnecessary. If iod-eosin were used by the canner instead of brom-eosin it might then be necessary to resort to Baeyer's test, for iod-eosin does not fluoresce and the color is not sufficiently distinctive to permit its recognition. Iod-eosin, however, is higher in price and not so well adapted for use in canned tomatoes, for a slight fluorescence is rather desirable in this case.

To recapitulate, the method we propose for recognizing the presence of brom-eosin in canned tomatoes is to strain off the solid matter and to the juice add hydrochloric acid and extract with ether. The ethereal solution is to be washed and shaken up with dilute solution of caustic soda. Should this solution be strongly colored, it is to be acidified and extracted with ether, the ether shaken up with dilute alkali and the alternate extractions with ether and alkali repeated till the presence or absence of eosin is demonstrated. The natural coloring matter of the tomato is not completely separated from acid solution by ether, nor is it completely abstracted from ether by alkali, so that by repeating the process sufficiently often it is separated to an extent sufficient to permit the recognition of eosin. Eosin is extracted quantitatively in both cases. Should it be desired to apply Baeyer's method in any case in which the presence of iod-eosin may be suspected it can be done by adding to the

<sup>1</sup> *Ber.*, 8, 146; *abs. Ztschr. anal. Chem.*, 1876, 15, 494.

final alkaline liquid some sodium amalgam, gently heating, and finally adding a drop or so of very dilute solution of potassium permanganate. In the presence of either iod-eosin or brom-eosin green fluorescence is developed. This test, however, presents no advantage in the case of brom-eosin.

## THE ELECTROLYTIC SEPARATION OF THE METALS OF THE SECOND GROUP.

BY SAMUEL C. SCHMUCKER.

Received July 8, 1893.

OF recent years the determination of metals quantitatively by the methods of electro-chemical analysis has grown into great popularity. The exceedingly accurate results, the simple forms obtained, and the ease with which it is possible to determine the absolute purity of the deposits all combine to make electrolytic methods highly desirable. Hitherto most of the operations have served simply to determine quantitatively the amount of one ingredient present, while comparatively less success has attended the separations of metals from each other. It is true that many valuable separations are known, the results of which have been published in the various chemical journals and in the few books devoted to the subject. But the list of separations of metals in the same group, and of separations of the different groups, is far from complete; and it is to this point that those chemists interested in electrolytic work are now giving their most earnest attention. Here the field seems at present likely best to repay the investigator.

As an example of a gap desirable to fill, I would cite the case of those metals known to analytical chemists as the *metals of the second group*, viz.: arsenic, antimony, tin, mercury (ic), lead, bismuth, copper, and cadmium. We have no electrolytic method serving for the separation of the first three from any of the later members. An examination of the literature of the subject would disclose to the student of electrolysis that should he encounter, for instance, a mixture containing copper, arsenic, antimony, and tin, he would find himself advised to abandon

the current and employ the usual gravimetric method of digesting with sodium sulphide to effect the separation of copper from the other constituents. Nor is this by any means a solitary example. It is true, individual separations have been made in this group. For example, Smith and Frankel<sup>1</sup> succeeded in separating copper from arsenic, both in cyanide solution and in ammoniacal solution in which the arsenic was in the form of pentoxide and there was much free ammonia. The results in this latter instance have been confirmed by McKay. Very recently, Smith and Wallace (*J. Anal. Appl. Chem.*, 7, 4) have printed an account of their successful separation, in very varying proportions, of copper from antimony, in alkaline tartrate solutions. These are the first successful results where antimony was present as more than a bare trace. Copper has never been separated from tin. Cadmium has no recorded separation from either antimony or tin; it has, however, been separated by Smith and Frankel from arsenic in cyanide solution. The case is in no wise better with either lead or bismuth. Solutions of either of these with any of the other three (As, Sb, Sn) have defied separation. Concerning mercury (ic) there is a little more to be said. If a mercuric solution contains also arsenic in the pentoxide form, and a decided excess of potassium cyanide, the mercury can be separated without difficulty. These results have suggested the question whether it is possible to find a general method suitable for the separation of any of the basic oxides of this second group from any or all of the acid oxides of the same group. This problem I have endeavored to solve. The method employed by Smith and Wallace for the separation of copper from antimony, suggested that in the alkaline tartrates might lie the key to the situation; and the separations from arsenic suggested, also, that it would be well to have the acid oxides in their highest state of oxidization. The results have fully justified my utmost expectation, and so far as they have been prosecuted, have been uniformly accurate. Inasmuch as we already have a separation of copper from arsenic, and of copper from antimony, my first attention was turned to the separation of

<sup>1</sup>*Am. Chem. J.*, 12, 428.

## COPPER FROM TIN.

A solution of copper sulphate was made containing 0.0999 grams of metallic copper in each portion measuring ten cc. About one-tenth of a gram (varying from 0.1020–0.1057 gram) of metallic tin was dissolved in hydrochloric acid, and bromine water added until the solution remained colored with the bromine to insure complete oxidation. I was led to suspect the presence of iron in the tin, and as this metal is deposited by the current from an alkaline tartrate solution, it became necessary to secure its removal. The tin solution was accordingly evaporated to dryness, taken up with caustic soda, the solution diluted, the iron filtered off, and the filtrate containing the tin (as sodium stannate) was neutralized with tartaric acid. To this solution four grams of tartaric acid were added and, as soon as this was thoroughly dissolved, ten cc. of ammonium hydroxide (sp. gr. 0.932). To this (after filtering off slight impurities brought in with the tartaric acid) ten cc. of the above mentioned cupric solution (containing 0.0999 grams copper) were added, the whole transferred to a platinum dish having a capacity of about 200 cc., and the solution diluted to 175 cc. with distilled water. A current, generated by five or six gravity cells coupled in series, was run through the solution, the anode being a flat platinum spiral. There was a voltameter also in the circuit. The precipitation was started at four P. M., and allowed to run during the night. The currents employed most successfully generated from 0.4 cc. to 1.2 cc. of electrolytic gas per minute. Immediately on interrupting the current, the liquid contents of the dish (which should smell quite strongly of ammonia) must be rapidly poured off, luke-warm distilled water poured into the dish, allowed to flow around the inside and gently emptied out. The washing with warm water should be repeated three or four times quite rapidly, and be followed by similar washings with small quantities of absolute alcohol. The dish can then be carefully dried on the edge of a warm plate, allowed to cool and weighed. Great care must be exercised during the drying to see that the dish does not get too warm, or the metal will readily oxidize, for the copper deposited from an alkaline tartrate solution does not have the lustrous sheen of that precipitated from solu-



tions containing free acid or potassium cyanide ; it has a velvety dark red appearance, but is thoroughly adherent to the dish. If the current is strong enough to generate one cc. of electrolytic gas per minute the precipitation is completed in five minutes. A decided excess of ammonia has no deleterious effect. The following examples will serve to illustrate the operation :

*Experiment 1.*—0.1087 gram of metallic tin was dissolved in hydrochloric acid, oxidized, evaporated to dryness, taken up with water and sodium hydroxide, filtered, neutralized with tartaric acid, four grams of solid tartaric acid and then ten cc. of ammonium hydroxide added. Ten cc. of the copper solution (0.0999 gram copper) were added, the whole transferred to a platinum dish, diluted to 175 cc., and the current applied. The current delivered 0.4 cc. of electrolytic gas per minute, and was allowed to act for seventeen hours. The deposit of copper weighed 0.1001 gram.

*Experiment 2.*—0.1039 gram was treated as above. Ten cc. of copper solution were used, four grams tartaric acid and fifteen cc. of ammonium hydroxide added, and a current generating one cc. of electrolytic gas per minute acted for fifteen and one-half hours. The precipitated copper weighed 0.0997 gram.

*Experiment 3.*—0.1044 gram of tin was treated as before : Four grams of tartaric acid and twenty cc. of ammonium hydroxide added, together with ten cc. of the copper solution. A current generating 1.2 cc. electrolytic gas per minute acted for five hours. The deposited metal weighed 0.0997 gram.

It having now been found possible to separate copper from arsenic, from antimony, and from tin, my attention was next turned to the possibility of separating copper from the other three collectively.

#### COPPER FROM ARSENIC, ANTIMONY, AND TIN.

Here, guided by the experience of Smith, Frankel, and Wallace, I decided to have the three acid oxides in their highest state of oxidation. Accordingly the solutions were made up as follows: A quantity of arsenious oxide weighing 3.3342 grams was dissolved in nitric acid (sp. gr. 1.3), and the solution evaporated to dryness. The arsenic acid thus formed was taken up with water, any slight impurities filtered off, and the filtrate

diluted to 250 cc. with distilled water. This gave a solution containing 0.1009 gram metallic arsenic in each ten cc. For the antimonious solution a portion of potassio-antimonious tartrate,  $C_4H_4(SbO)KO_6 + \frac{1}{2}H_2O$ , was dissolved in water, diluted largely, and then boiled with addition of bromine water until the solution remained discolored for a considerable time by the bromine, thus indicating the complete oxidation of the antimony. The addition of a small quantity of tartaric acid prevented the slight tendency to precipitation of oxysalts. The solution was filtered and diluted to 250 cc., thus giving 0.1024 gram metallic antimony in each ten cc. The tin solution was prepared as described under the section on copper and tin, and was made of such a strength as to contain 0.1031 gram metallic tin to every ten cc. The copper solution was made by dissolving a little more than twenty grams of copper sulphate and diluting to 500 cc. Ten cc. of this solution as determined by direct trial contained 0.1016 gram metallic copper.

The solution which proved best for the separation contained eight grams of tartaric acid, thirty-one cc. of ammonium hydroxide, and ten cc. of each of the solutions of copper, antimony, arsenic, and tin described above. Five hours proved sufficient time, and a current generating 0.8 cc. electrolytic gas per minute proved of sufficient strength to effect a thorough precipitation of the copper entirely free from any of the other three metals. The copper has the same appearance as when separated from tin, and must be washed and dried in the same way. It is, however, absolutely necessary to keep the quantity of tartaric acid and of free ammonia as high as indicated or antimony to the amount of fully one-half of that present will be precipitated. I give the following results:

*Experiment 1.*—Eight grams of tartaric acid were dissolved in water, thirty cc. of ammonium hydroxide added, and the solution filtered. To this were added ten cc. of each of the solutions of arsenic, antimony, tin, and copper (0.1016 in ten cc.) previously mentioned, and the solution diluted to 175 cc. The current generated 0.8 cc. electrolytic gas per minute, and was allowed to act for five hours. The precipitated copper weighed 0.1019 gram.

*Experiment 2.*—Exactly the same quantities as in 1 were exposed with the same strength of current and for the same length of time. This resulted in the deposition of 0.1010 gram of metallic copper instead of 0.1016 gram.

Having thus succeeded in the separation of copper, I next directed my attention to cadmium, and as antimony seemed to give the most trouble I began with the separation of

#### CADMIUM FROM ANTIMONY.

The antimony solution was the one previously described. The cadmium solution was the nitrate and contained 0.0916 gram of the metal in ten cc. of solution as determined by electrolytic deposition from the cyanide solution. There is only one difficulty presented in this separation, and that is that the current must be weak, or the deposited cadmium will be too spongy to wash. Accordingly, it is necessary to allow the current to act through the night. The deposit of metal shows a tendency to form spongy masses here and there. These can be washed without loss if care be exercised in pouring the wash water on and off. The dish containing the deposit is washed with water simply—the washing with alcohol being unnecessary—and then dried on the edge of the hot plate. As actual results I give the following:

*Experiment 1.*—Five grams of tartaric acid were dissolved in hot water, fifteen cc. of ammonium hydroxide were added, and the solution filtered free from impurities introduced by the acid. Ten cc. of the antimony solution and ten cc. of the cadmium solution (0.0916 gram metallic cadmium) mentioned above were added, the whole transferred to a platinum dish, diluted to 175 cc., and the current allowed to act over night. The cadmium was washed with hot water and dried. It weighed 0.0920 gram.

*Experiment 2.*—The solution here was made up in the same way as in the preceding experiment. The current gave 0.3 cc. electrolytic gas per minute. It acted over night. The cadmium deposit weighed 0.0925 gram.

*Experiment 3.*—The solution was just the same as in the last case. The current gave 0.4 cc. electrolytic gas per minute and acted for sixteen hours. The deposit of metallic cadmium weighed 0.0925 gram.

## CADMIUM FROM TIN.

In this case the tin solution was the same as that employed in the separation of arsenic, antimony, and tin from copper, and indeed, throughout the rest of these trials the arsenic solutions (0.1009 gram metallic arsenic in ten cc.), the tin solutions (0.1031 gram metallic tin in ten cc.), and the antimony solutions (0.1024 gram of antimony in ten cc.) are the same. The separation presents no difficulties and the metal is deposited in good form if the precaution previously mentioned is observed, namely, to use a long-continued weak current. The metal should be washed with hot water only, and dried on the edge of a warm plate.

*Experiment 1.*—Five grams of tartaric acid were dissolved in water, fifteen cc. of ammonium hydroxide added, then ten cc. of the tin solution, and ten cc. of the cadmium solution (0.0916 gram). This was diluted to 175 cc. in the platinum dish, and a current liberating 0.1 cc. of electrolytic gas per minute allowed to act upon the mixture for eighteen and one-half hours. The cadmium deposit was washed with hot water, dried and weighed. It equaled 0.0914 gram.

*Experiment 2.*—The conditions and quantities were here just the same as in the last experiment save that the current delivered 0.2 cc. of electrolytic gas and was allowed to act for eighteen hours. The cadmium weighed 0.0918 gram.

## CADMIUM FROM ARSENIC.

The solutions employed in this case were those used previously. The amount of tartaric acid was five grams and of ammonium hydroxide fifteen cc. This quantity proved the best for all separations where but two metals were present and was adhered to under these circumstances throughout the rest of the work. When more than two elements are present it becomes necessary to increase the amounts of tartaric acid and of ammonium hydroxide to eight grams and thirty cc. respectively. The tartaric acid was dissolved in water as before, the ammonium hydroxide added, followed by the arsenic and cadmium, the solution transferred to the platinum dish, diluted to 175 cc., and then electrolyzed. The deposit differed in no wise from that obtained in the separation of cadmium from tin.

*Experiment 1.*—Five grams of tartaric acid were dissolved in water, fifteen cc. of ammonium hydroxide were added, followed by ten cc. of the cadmium solution (= 0.0916 gram cadmium), and ten cc. of the arsenic solution. The mixture was introduced into a platinum dish, diluted to 175 cc., and a current that gave 0.3 cc. of electrolytic gas per minute allowed to act for a period of sixteen hours. The cadmium deposit weighed 0.0913 gram.

*Experiment 2.*—Like quantities were taken and treated in the same manner, except that the current delivered 0.2 cc. of electrolytic gas per minute. It acted sixteen hours. The cadmium deposit weighed 0.0921 gram.

#### CADMIUM FROM ARSENIC, ANTIMONY, AND TIN.

The solution was now made up by combining the arsenic, antimony, and tin with the cadmium. The tartaric acid was increased to eight grams and the ammonium hydroxide to thirty cc. The cadmium separated from the three differed in no respect from that separated from any one. It had the same appearance and washed and dried in the same way.

*Experiment 1.*—Eight grams of tartaric acid were dissolved in water, thirty cc. of ammonium hydroxide were added, followed by ten cc. each of arsenic, antimony, tin, and cadmium solutions. The current liberated 0.25 cc. of electrolytic gas per minute and acted for eighteen hours. The metallic cadmium weighed 0.0915 gram.

*Experiment 2.*—The same quantities were used as in experiment 1. The current gave 0.4 cc. of electrolytic gas per minute and acted sixteen hours. The deposit of cadmium weighed 0.0920 gram.

*Experiment 3.*—Same quantities were used. The current gave 0.3 cc. of electrolytic gas per minute and precipitated 0.0918 gram cadmium.

Copper and cadmium having yielded thus easily to the current in the presence of arsenic, antimony, and tin in ammonium tartrate solutions, my attention was next turned to bismuth.

#### BISMUTH FROM ARSENIC.

The solution was made by dissolving 5.8 grams of bismuth nitrate in water acidulated with enough nitric acid to prevent the formation of basic salts. The solution was diluted to 400 cc.

and ten cc. taken for the determination of the bismuth. The metal was precipitated from the alkaline tartrate solution and weighed 0.0518 gram. The practice had now become uniform of adding five grams of tartaric acid and fifteen cc. of ammonium hydroxide when two metals were present, and eight grams of acid and thirty cc. of ammonium hydroxide when four metals were in the same solution. The solution was made up as in all preceding cases and the process differed in no way until the washing began. Bismuth does not form so compactly on the dish as cadmium does or even as copper from the alkaline tartrate solution. Accordingly great care was necessary in the washing. In drying, too, it seemed to oxidize with very little heating. Therefore, when the deposition was complete the anode was raised, the liquid gently but quickly decanted from the deposited bismuth, and the wash water gently poured on and off. This latter was repeated three or four times, and was followed by three or four washings with absolute alcohol. The dish was placed on a very moderately heated plate and the evaporation of the alcohol facilitated by gentle blowing. It is best to use a long-continued weak current for bismuth or the deposit will be spongy and loose, rendering washing difficult.

*Experiment 1.*—The solution contained five grams of tartaric acid, fifteen cc. of ammonium hydroxide, 0.1009 gram metallic arsenic, and 0.0518 gram of bismuth. It was diluted to 175 cc. The current acted sixteen hours and gave 0.3 cc. of electrolytic gas per minute. The precipitated bismuth weighed 0.0514 gram.

#### BISMUTH FROM ANTIMONY.

Here the procedure was exactly similar to that described under the separation of bismuth from arsenic. The precipitated metal resembled that obtained in the preceding experiment.

*Experiment 1.*—The solution contained five grams of tartaric acid, fifteen cc. of ammonium hydroxide, 0.1024 gram of antimony, and 0.0518 gram of bismuth. It was diluted to 175 cc. The current gave 0.22 cc. of electrolytic gas per minute. It acted sixteen and one-half hours. The deposit of metallic bismuth weighed 0.0513 gram.

## BISMUTH FROM TIN.

The method of procedure was just the same here as in the separation of antimony or of arsenic from bismuth. The precipitated bismuth was treated as heretofore and had the same appearance.

*Experiment.*—The solution contained five grams of tartaric acid, fifteen cc. of ammonium hydroxide, 0.1031 gram of metallic tin and 0.0518 gram of metallic bismuth. It was diluted with distilled water to 175 cc. The acting current gave 0.2 cc. of electrolytic gas per minute; time, sixteen and one-half hours. The bismuth deposit weighed 0.0514 gram.

## BISMUTH FROM ARSENIC, ANTIMONY, AND TIN.

The procedure was again just as before. The bismuth precipitated readily and in as clean a form as when separated from each of the metals singly.

*Experiment.*—The solution contained 0.0518 gram of bismuth, 0.1009 gram of arsenic, 0.1024 gram of antimony, 0.1031 gram of tin, eight grams of tartaric acid, thirty cc. of ammonium hydroxide, and was diluted to 175 cc. The current gave 0.2 cc. of electrolytic gas per minute and was allowed to act for sixteen and one-half hours. The bismuth, after washing and drying, weighed 0.0513 gram.

The method adopted by me having proved successful in the separation of copper, cadmium, and bismuth from the metals forming acid oxides, I next applied it to the study of mercury in its bivalent form. About seven grams of mercuric chloride were dissolved in distilled water and diluted to 500 cc. Ten cc. of this solution proved to contain 0.0933 gram of metallic mercury. I first undertook the separation of

## MERCURY FROM TIN.

There was a doubt in my mind whether the mercuric compound could be made up in alkaline tartrate solution when there was so much free ammonia present. I found, however, that if the mercuric chloride solution be added to the tartaric acid solution before the addition of the ammonia there is little likelihood of trouble, though even then the double compound sometimes forms, especially if the solutions be not dilute. But

if care be exercised the mercuric salt may be added last. If the solution is well diluted and the mercuric salt added with constant stirring all remains in solution very nicely. The mercury and tin were then combined with the tartaric acid and ammonia, the solution diluted, and the current passed. The precipitation is quite rapid even with a fairly weak current, and the metal separates as a lustrous coating having a very slight tendency to drops. The mercury is washed with very warm water three or four times and then dried by keeping the dish in the warm hand and blowing gently into it to facilitate the evaporation. Any attempt to dry it on the plate is attended with very considerable risk of vaporizing a portion of the mercury.

*Experiment.*—Ten cc. of the mercuric chloride solution (= 0.0933 gram metallic mercury, ten cc. of tin solution, five grams of tartaric acid, and fifteen cc. of ammonium hydroxide were united and diluted to 175 cc. The current gave 0.2 cc. of electrolytic gas per minute and was continued for six hours. The mercury deposit weighed 0.0930 gram.

#### MERCURY FROM ARSENIC.

The solution contained 0.0933 gram of mercury, 0.1009 gram of arsenic, five grams of tartaric acid and fifteen cc. of ammonium hydroxide. It was diluted to 175 cc. The current gave 0.33 cc. of electrolytic gas per minute, acted for five hours, and deposited 0.0928 gram of metallic mercury.

#### MERCURY FROM ANTIMONY.

*Experiment.*—The solution contained 0.1024 gram of antimony in addition to the mercury, also five grams of tartaric acid and fifteen cc. of ammonium hydroxide. It was diluted to 175 cc. with water. The current gave 0.5 cc. of electrolytic gas per minute. It acted for six hours and precipitated 0.0932 gram of metallic mercury.

#### MERCURY FROM ARSENIC, ANTIMONY, AND TIN.

The solution was made up in the same manner as in the three preceding separations, save for the increase of tartaric acid and of ammonium hydroxide. There was, however, a difference in the nature of the deposited mercury. A part of it gathered as in the other cases in a lustrous coating on the sides of the dish,



but in addition to this there was quite a considerable amount of mercury in the form of drops so small as to be almost pulverulent. This rendered washing exceedingly difficult. The fluid contents of the dish, after the anode has been raised, are carefully decanted from the powder, boiling water added, allowed to flow around the dish, and again very carefully decanted. This was repeated six or seven times, never draining off the last drops to avoid loss of the mercury. If this care is taken there is no difficulty about good results, but the slightest haste results in the loss of mercury. Naturally when that much water remains on the mercury the evaporation from the heat of the hand is a most tedious, but the only safe, process.

*Experiment 1.*—The solution contained 0.0933 gram of mercury, 0.1009 gram of arsenic, 0.1024 gram of antimony, 0.1031 gram of tin, eight grams of tartaric acid, thirty cc. of ammonium hydroxide, and was diluted to 175 cc. The current gave 0.5 cc. of mixed gases per minute. It acted for sixteen hours and precipitated 0.0935 gram of mercury.

*Experiment 2.*—The conditions were the same as in the first experiment. The current gave 0.4 cc. of electrolytic gas per minute and precipitated 0.0933 gram of metallic mercury.

I made no attempt to separate lead from arsenic, antimony or tin.

In conclusion, I would acknowledge my indebtedness to Prof. Edgar F. Smith, at whose suggestion and under whose supervision the above studies were brought to completion.

UNIVERSITY OF PENNSYLVANIA,  
JULY 1, 1893.

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## THE ACTION OF GASES UPON METALLIC MOLYBDENUM AND TUNGSTEN.

BY EDGAR F. SMITH and VICKERS OBERHOLTZER.

Received July 12, 1893.

HAVING prepared these two metals with care and believing them to possess a high degree of purity, we conceived that it might be of interest to observe their behavior when exposed, at more or less elevated temperatures, to the influence of different gases. We first studied their conduct in an atmosphere of carbon mon-

oxide. The temperature was raised to a red heat, but no reaction whatever occurred. Again, both metals remained unaffected when heated to redness in a brisk current of dry ammonia gas. The period of time during which the gases mentioned were conducted over the heated metals was in each case one hour.

Our next step was to ascertain how each metal would deport itself in an atmosphere of carbonyl chloride ( $\text{COCl}_2$ ). This compound was prepared by passing well-dried chlorine gas together with an excess of carbon monoxide through a hard glass tube filled with bone black, the latter being heated to redness. The air in the tube had been displaced by hydrogen and the metal ignited in this gas, after which carbon dioxide was introduced to displace the hydrogen, and the tube then connected with the apparatus from which the carbonyl chloride was evolved.

*Action of Carbonyl Chloride upon Molybdenum.*—The metal was contained in a porcelain boat. The reaction began at a temperature varying from 150 to 200° C. A dark red colored vapor was produced and condensed in drops in the cooler portions of the tube. The action of the gas was continued until no more molybdenum remained in the boat. As soon as the combustion tube had become perfectly cool the liquid in the anterior portion was quite stiff and jelly-like. On coming in contact with the air it immediately solidified, and its surface was covered with a light, white, woolly substance. This solid mass was subjected to sublimation in currents of carbon dioxide, carbon monoxide, and nitrogen with apparently no attendant decomposition, but we found that, after sublimation had occurred in an atmosphere of carbon monoxide, the boat contained a hard, black residue; its analysis revealed the presence of 32.79 per cent. of metallic molybdenum. The quantity of this material was so slight that we consumed much time in preparing a sufficient amount (0.0663 gram) for this single determination and we were forced to leave the examination for chlorine and carbon go by default. The jelly-like compound, mentioned above, melts below 100° C. Under certain conditions, not clearly understood by us, the product is solid from the very outset, is brittle and can be easily scraped from the sides of the tube upon which it

had been deposited. It apparently is more stable, too, than the jelly-like mass. Both modifications decompose very energetically on coming in contact with water, carbonyl chloride or hydrochloric acid gas being simultaneously liberated. This behavior caused us much trouble in the estimation of the chlorine.

We analyzed both modifications, and give a few results obtained with the solid, non-crystalline and reddish-brown material.

*Molybdenum Determination.*

				Per cent.
1.—0.1636	gram substance	gave	0.0873 gram $\text{MoO}_3$	= 35.59
2.—0.1182	"	"	0.0626 "	= 35.29
3.—0.3867	"	"	0.2073 "	= 35.74

The jelly-like form contained a little less molybdenum, but approximated the figures just recorded.

The mean of these molybdenum percentages is 35.54 per cent.

*Chlorine Determination :*

				Cl per cent.
1.....	0.0927	gram substance	gave 0.2015 gram $\text{AgCl}$	= 53.75
2.....	0.0321	"	" 0.0694 "	= 53.46
3.....	0.1864	"	" 0.3940 "	= 52.27

The mean of these results is 53.16 per cent. It may be well to add that in the third analysis a slight loss of chlorine was sustained when the material was brought in contact with water. Now, upon summing up the results we encounter a difference of 11.30 per cent., which perhaps may be due to oxygen. Granting that such is the case we then deduce an atomic ratio of one Mo, two O, and four Cl. This corresponds with no known molybdenum oxychloride, and we have further to add that, upon taking material which had been sublimed and re-sublimed in an atmosphere of nitrogen and which we had every good reason to presume was no longer accompanied with carbonyl chloride, and subjecting this apparently pure compound to analysis, viz., burning it in an atmosphere of oxygen and proceeding as in an ordinary combustion for the estimation of carbon, we several times obtained five per cent. of carbon monoxide. If the product under examination were a true and pure molybdenum carbonyl derivative,  $\text{Mo}(\text{CO})\text{Cl}_4$ , we should have gotten about eleven per cent. of carbon monoxide. Qualitative tests, *e. g.*, burning of the compound in pure oxygen, and conducting the gases into lime water

also revealed the presence of carbon monoxide. The product is not a pure carbonyl derivative, but we are firmly of the opinion that such a derivative is present in the mixture and that in all probability the contaminating or admixed substance is  $\text{MoOCl}_2$ , for we frequently noticed that the reddish-brown powder gradually assumed a greenish hue as traces of air came in contact with it. Assuming that what we analyzed was a mixture of a molecule of molybdenum oxychloride,  $\text{MoOCl}_2$ , and a molecule of molybdenum carbonyl,  $\text{Mo}(\text{CO})\text{Cl}_2$ , we can get theoretical figures that closely approximate the results that we actually obtained by analysis. It is our purpose as time and opportunity allow, to follow this line of investigation further, and strive either to isolate the carbonyl derivative and prove its actual existence, or to show some reason for the peculiar results we have obtained in our present study. Abandoning, then, all further speculation as to the nature of our molybdenum product we may pass to the

*Action of Carbonyl Chloride upon Tungsten.*—The phosgene was prepared as before and the metal exposed just the same as in the case of the molybdenum. On raising the boat and its contents to a low red heat, at the same time conducting the gas in a rapid current through the tube, orange-red colored, needle-shaped crystals sublimed beyond the boat. In the course of an hour all the metallic tungsten had disappeared, leaving a black metallic residue in the boat. The combustion tube and its contents were allowed to cool. The orange-red colored sublimate was removed and sublimed in an atmosphere of nitrogen gas. An examination of the black residue contained in the boat proved it to be *pure carbon*. In appearance it resembled soot. The analyses of the purified orange-colored derivative show that it was tungsten oxytetrachloride.

*Tungsten Determination:*

				W per cent.
1.....	0.1076	gram material gave	0.0729 gram $\text{WO}_3$	= 53.76
2.....	0.0300	" " "	0.0438 " "	= 54.30

*Chlorine Determination:*

				Cl per cent.
1.....	0.1120	gram material gave	0.1935 gram $\text{AgCl}$	= 42.72
2.....	0.2114	" " "	0.3577 " "	= 41.25

In determining the chlorine we ignited the material in an air current and conducted the gases through a silver nitrate solution. The theoretical requirements of the compound  $\text{WOC}_l$  are 53.80 per cent. W and 41.52 per cent. Cl. These results leave little doubt as to the action of carbonyl chloride upon heated metallic tungsten and indicate, too, that an oxychloride could well be present in the molybdenum product that we have briefly described in the preceding paragraphs.

We next undertook the study of the deportment of the two metals when heated in the vapor of sulphur chloride ( $\text{S}_2\text{Cl}_2$ ). To this end a small flask containing liquid chloride of sulphur was connected with a hard glass tube, about twenty inches long which terminated in a receiver. Carbon dioxide was first passed through the entire apparatus and when all the air had been expelled the flask containing the sulphur chloride was gently heated and the current of carbon dioxide continued. In this manner the vapor was brought in contact with the metals which were exposed in boats. The excess of sulphur chloride was condensed and collected in the receiver.

*Action of Sulphur Chloride in Gas Form upon Molybdenum.*—

At a low temperature a yellowish-white, crystalline sublimate appeared, and sulphur separated. The crystalline product did not contain sulphur. As soon as it ceased forming it was removed, and the heat increased until the boat and its contents approached a red heat, when further reaction set in. A reddish-brown colored, and perfectly amorphous sublimate made its appearance. The slow current of carbon dioxide, passed continuously through the apparatus, carried off the excessive sulphur chloride. A white, very volatile and woolly product was produced simultaneously with the amorphous brown material; the latter was freed from the former by gently heating in a current of carbon dioxide. The amorphous product was heated several times in carbon dioxide, indeed as often as seemed necessary to eliminate any sulphur chloride that might be mixed with it. Sublimation in an atmosphere of carbon monoxide was tried, but partial decomposition ensued with the evident formation of a black mass resembling molybdenite very much in general appearance and behavior. The reddish-brown material proved to

be rather stable in the air and insoluble in water and in the alkalis. Concentrated nitric acid dissolved it completely after standing for some time. The sulphur content was determined by heating a weighed quantity of the substance in a current of oxygen and passing the sulphur dioxide that resulted through hydrochloric acid containing bromine. The sulphur was finally weighed as barium sulphate.

## ANALYSIS.

*Molybdenum Determination :*

						Mo per cent.
1	.....	0.1009	gram substance	gave	0.0680	gram $\text{MoO}_3 = 44.93$
2	.....	0.0811	" " "	"	0.0556	" " = 45.69
3	.....	0.1094	" " "	"	0.0759	" " = 44.78

The mean of these percentages is 45.13 per cent.

*Chlorine Determination :*

						Cl per cent.
1	.....	0.1076	gram substance	gave	0.1333	gram $\text{AgCl} = 30.63$
2	.....	0.1185	" " "	"	0.1422	" " = 29.70

The mean of these results is 30.16 per cent. Cl.

*Sulphur Determination :*

						S per cent.
1	.....	0.1090	gram substance	gave	0.1945	gram $\text{BaSO}_4 = 24.53$
2	.....	0.1185	" " "	"	0.3289	" " = 24.37

The mean of results is 24.45 per cent. S.

The formula that may be deduced from these figures is  $\text{Mo}_5\text{S}_4\text{Cl}_4$ . Its theoretical requirements are 45.47 per cent. Mo, 24.25 per cent. S, and 30.27 per cent. Cl, with which our analytical results accord quite well. We must evidently regard this as an unsaturated molybdenum derivative, which can be explained by the assumption that sulphur has been substituted for equivalent amounts of chlorine in five molecules of molybdenum pentachloride.

*The Action of Sulphur Chloride in Gas Form upon Tungsten.—*

A dark-red crystalline sublimate is produced when sulphur chloride vapors are conducted over gently heated tungsten.

This compound is readily volatilized and is soluble in sulphur chloride, from which it is rather difficult to free it. The first sublimate was sublimed and re-sublimed until only a crystalline

product remained. This proved to be very unstable in the air, lost color and was decomposed quite energetically by water, liberating hydrogen sulphide and separating tungstic acid. The sulphur content was estimated in the same manner as with the preceding molybdenum derivative, while the tungsten and chlorine were determined in the ordinary way, care being exercised with the latter so that as little loss as possible would be sustained when the compound was brought in contact with water.

## ANALYSIS.

*Tungsten Determination :*

					W per cent.
1.....	0.1157	gram substance	gave 0.0618	gram $WO_3$	= 42.38
2.....	0.0973	" "	" 0.0510	" "	= 41.59
3.....	0.1507	" "	" 0.0814	" "	= 42.19
4.....	0.1537	" "	" 0.0838	" "	= 42.19

The mean of these percentages is 42.12 per cent. W.

*Sulphur Determination :*

					S per cent.
1.....	0.1699	gram substance	gave 0.3136	gram $BaSO_4$	= 25.38
2.....	0.1737	" "	" 0.3236	" "	= 26.03

The mean percentage is 25.70.

*Chlorine Determination :*

					Cl per cent.
1.....	0.0631	gram substance	gave 0.0734	gram $AgCl$	= 31.93
2.....	0.0988	" "	" 0.1274	" "	= 31.88
3.....	0.1478	" "	" 0.1867	" "	= 31.24

The mean of these results equals 31.68 per cent.

Employing the means of the three determinations we deduce as the empirical formula of this new derivative,  $W_2S_3Cl_4$ , which we would express as follows:  $W_2S_3Cl_4 + 2 S_2Cl_2$ . The theoretical requirements of this compound are 42.03 per cent. W, 25.57 per cent. S, and 32.42 per cent. Cl. Like the molybdenum derivative it may be viewed as an unsaturated sulphochloride derived from two molecules of the pentachloride by the substitution of sulphur for chlorine and in addition combined with sulphur chloride.

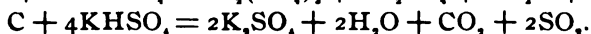
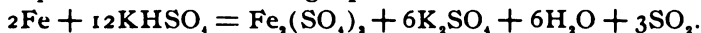
The study of the deportment of molybdenum and tungsten in atmospheres of other gases will be continued in this laboratory.

## A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF CARBON IN IRON AND STEEL.<sup>1</sup>

BY OTTO PETTERSON AND AUGUST SMETT. TRANSLATED BY GEO. SCHOLL,  
CATASAUQUA, PA.

BY dissolving iron in diluted acids or in other solvents employed for this purpose, as cupric sulphate, cupric chloride, mercuric chloride, even free iodine, a part of the carbon escapes as volatile hydrocarbons. The authors affirm that this happens also by heating iron in dry hydrochloric acid gas. Ullgren based his well-known method on the oxidation of carbon by chromic acid and used potassium bichromate and sulphuric acid for the quantitative determination of carbon in iron. But even in presence of such a strong oxidizing agent hydrocarbons escape unoxidized and the method was only made accurate through its modification by Särnström (*Jernkontorets Ann.*, 1884, 385) by conducting the generated gaseous products either over glowing cupric oxide or mixed with air through a narrow, strongly-glowing platinum tube and absorbing the carbon dioxide and determining it by weighing. According to Adolf Tamm (*Jernkontorets Ann.*, 1874, 157) just as accurate a determination of the carbon by weighing as carbon dioxide can be made by burning iron in a current of dry oxygen gas.

The authors have for some time endeavored to complete a new method for dissolving iron, which contains carbon, the solution to be effected in the dry way. After several experiments with melting sodium pyro and metaphosphate or borax, they succeeded in finding a suitable solvent in potassium pyrosulphate, at a temperature at which the purest mercantile potassium bisulphate fuses quietly without giving off gas bubbles. The iron as sheet or drillings dissolves very quickly and completely, the solution getting dark red. Besides carbon dioxide and sulphur dioxide small quantities of hydrocarbons are formed, which even at this high temperature escape unoxidized. The reactions can be expressed in the following equations :



<sup>1</sup> *Jernkontorets Ann.*, from the *Ztschr. anorg. Chem.*



tached to the neck of the flask D, the burner removed and a protection tube, F, (filled with cotton and potassium hydroxide) is inserted in the reservoir E. The flask is then connected with the tube C as quickly as possible, the connections are made air tight with copper wire, and when the stream of air passes evenly through the apparatus, the fusion of the iron begins. A sheet of 0.5 gm. dissolves in seven minutes; the generation of the gases is rapid and even and ceases instantly when the reaction is finished. The current of air is allowed to pass through the apparatus for ten minutes after the disappearance of the last particle of iron, so as to carry the last trace of generated carbon dioxide into the solution of baryta and to absorb it with certainty.

Professor Petterson has constructed an apparatus for volumetric determination of the carbon dioxide, which gives results as accurate as can be desired. He therefore did not use a method for the determination of the carbon dioxide by weight in the present case, but the above mentioned apparatus. The following operations are necessary to connect the absorption flask D with it: After the carbon dioxide absorption is complete, flask D and tube C are disconnected, and tube f is washed with boiling water and removed. To be sure that there is no sulphur dioxide carried into the solution of baryta by the current of air, it is only necessary to add a couple of small drops of potassium permanganate and shake; if the liquid assumes a rosy color, only carbon dioxide has been absorbed. The flask is then filled with boiled, distilled water up to the narrow side tube, the so-called hydrogen generator (an iron wire, several centimeters long and inserted into a capillary glass tube, for the purpose of preventing the bumping of the liquid when boiling) is introduced, ten cc. hydrochloric acid are put in the reservoir E, D is connected with Petterson's apparatus for the determination of carbon dioxide and the determination completed after his description (*Ber. d. chem. Ges.*, **23**, 1402, 1890).

From the amount of carbon dioxide obtained by this method a small quantity has to be deducted, which is contained in the reagents, especially in the hydrochloric acid. The correction is found by making several experiments in the apparatus without using iron. The authors mention four of their experiments.

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which gave 0.246 to 0.249, an average of 0.248 cc. carbon dioxide at 760 mm. and 0° C. The correction therefore is a constant quantity equal to 0.248 cc. Every chemist who uses this method, has of course to ascertain this factor for himself.

In this method 0.10 cc. carbon dioxide equals 0.01 per cent. carbon in the iron. It is easily seen that the small variation of the carbon dioxide in the reagents cannot have any influence on the accuracy of the determination.

The authors give the results of their carbon determinations in some normal irons, which they received through Professor Åkerman from the collection of the Academy of Mines of Stockholm and which come from Miller, Metcalf and Parkin, Pittsburg, Pa. The four samples contained the following quantities of carbon in 100 parts :

	1.	2.	3.	4.
1.....	1.421	0.817	0.447	0.163
2.....	1.419	0.810	0.451	0.169
3.....	1.458	0.817	0.455	0.175
4.....	1.432	0.813	0.451	0.164
5.....	1.417	....	0.442	0.169
6.....	1.431	....	0.444	....
Average....	1.430	0.814	0.448	0.168

Whenever iron which contains graphite is analyzed by this method, there is left a residue of fine shining scales of graphite, swimming on the fusion ; these can be filtered off after solution of the fusion in hydrochloric acid and taken up by a platinum filter with asbestos (figures 4 and 5). The authors weighed the filter first with the graphite, and then after the burning of the graphite in a current of air loaded with nitrous gases (figure 5) and obtained the weight of the graphitic residue as mentioned in *Ber. d. chem. Ges.*, **23**, 1401, 1890.

## RECENT METHODS IN FERTILIZER ANALYSIS.

EDITED BY EDWIN J. HALEY, A. M.

STOCK'S rapid method for the determination of nitrogen in organic compounds (*Analyst*, **17**, No. 194, 109) has aroused more than passing notice and discussion. Briefly, the original method is as follows: From 0.5-1 gram of substance is mixed in

tached to the neck of the flask D, the burner removed and a protection tube, F, (filled with cotton and potassium hydroxide) is inserted in the reservoir E. The flask is then connected with the tube C as quickly as possible, the connections are made air tight with copper wire, and when the stream of air passes evenly through the apparatus, the fusion of the iron begins. A sheet of 0.5 gm. dissolves in seven minutes; the generation of the gases is rapid and even and ceases instantly when the reaction is finished. The current of air is allowed to pass through the apparatus for ten minutes after the disappearance of the last particle of iron, so as to carry the last trace of generated carbon dioxide into the solution of baryta and to absorb it with certainty.

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a small beaker with ten cc. sulphuric acid (sp. gr. 1.84), and five grams of native manganese dioxide (passed through a thirty-six mesh sieve). The flask is heated on an iron plate until the contents assume a dark green color, due to the formation of man-ganic sulphate. This indicates the end reaction. The flask is cooled, water added, and an excess of sodium hydroxide in solu-tion (twenty grams sodium hydroxide for ten cc. sulphuric acid) is added, and the distillation and titration conducted in the usual way.

The new method can not be considered simply a modification of Kjeldahl's process, for the principal oxidant in the latter process is sulphuric acid while manganese dioxide is the oxi-dizing reagent in Stock's process. The author of the method claims to have oxidized a sample of bone meal in three minutes and determined the nitrogen in fifty minutes from the time of weighing out.

Manures and other substances containing a large amount of chlorides can not be treated directly by this method. The chlorides must first be decomposed by heating with sulphuric acid alone for twenty minutes and the manganese oxide can then be added at once and the process continued as usual.

The following are experimental results obtained by Stock :

	Nitrogen by new method.	Nitrogen by combustion.
Bone meal .....	3.64 per cent.	3.54 per cent.
Cotton cake.....	3.49 "	3.69 "
Fish flesh.....	7.51 "	7.41 "

The apparatus used by Stock in his first experimentation con-sisted of a copper boiler, 600 cc. capacity, closed by a screw cap and India rubber washer. This cap carries a topped funnel for the introduction of sodium hydroxide solution, and a wide evolu-tion tube to serve as a reflux tube in case of frothing. The evolution tube is closed by a rubber stopper carrying a tube bent at such an angle as will permit its passing down the cen-ter of a Wurtz flask, which serves as a washing flask for the vapors from the copper boiler. Both boiler and flask are pro-vided with burners and both must be kept boiling throughout the experiment. The Wurtz flask is in turn connected with a fourteen-inch Liebig condenser, set vertically, and this termi-

nates in a 500 cc. receiving flask fitted with a guard tube filled with beads through which the standard acid is run into the receiver. The open ends of the tubes are all ground off at an acute angle so as to prevent the formation of piston-drops.

Later (*Analyst*, 18, No. 203, 58) Stock simplified his apparatus by dispensing with one of the two Bunsen burners and made it consist of a Wurtz flask, 150 cc. capacity, the tube from which runs into the condenser. The flask is kept at boiling point by the ammoniacal steam from the distilling flask. By this simplification the conveyance of sodium hydrate into the distillate is prevented.

The chief objection raised to the above method was the loss of nitrogen due to progressive oxidation finally producing nitric acid.

Skertchly (*Analyst*, Nov., 1892) gave as the results of his experimentation with the method that it failed on account of the loss of nitrogen due to the mixture of sulphuric acid and manganese dioxide acting upon nitrogenous substances like sulphuric acid and potassium permanganate causing loss of ammonia.

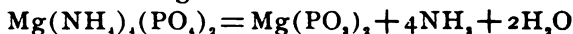
Stock explained Skertchly's loss of ammonia to be due to a want of division of the samples whence nitrogen was left unconverted, and also to a non-conformity to the process itself, for Skertchly used as an oxidant manganese dioxide containing 40.56 per cent. manganese dioxide while Stock used eighty to ninety-seven per cent. manganese dioxide. Hehner holds it is immaterial whether manganese dioxide is inferior or not, provided it contains sufficient dioxide to oxidize the substance; and as the point of complete oxidation is denoted by the green color there should be no reason for loss of nitrogen due to incomplete oxidation.

Böttcher (*Lands. Ver. Stat.*, 41, 170-4) recommends the Jodlbauer modification for the determination of nitrogen in nitrates and Wilfarth's modification (addition of metallic oxides during digestion) for materials difficult to decompose, such as ground bone, ground fish, etc. He found that the addition of mercury gives a higher result in some analyses than copper and prefers to add 1.5 grams of zinc dust instead of potassium sulphide and zinc dust in the distillation with sodium hydroxide.

The zinc dust alone suffices to free the ammonia from the mercurio-ammonium compounds.

Winton, of the Connecticut experiment station, in a bulletin of June, 1892, proposes the following modified Gunning-Kjeldahl method in presence of nitrates: 0.3 to 1 gram of material is digested with thirty cc. Scovell's salicylic acid mixture for two hours. Two grams of zinc dust are added and a slow heat applied. Ten grams of potassium sulphate are added and the boiling continued until the solution is colorless or straw-colored, due to the presence of iron. As the mixture begins to solidify on cooling, water is added, and the distillation with sodium hydroxide carried on in the usual manner. The results were very satisfactory as compared with the Scovell-Jodlbauer method. The greatest discrepancy was 0.1 per cent. and the average difference between the two methods was 0.05 per cent.

Some important experiments have been made and interesting results been secured on the reliability of the determination of phosphoric acid as magnesium pyrophosphate by the molybdic acid method. Neubauer (*Ztschr. anorg. Chem.*, 1892, 2, 45) after exhaustive experimentation concluded that a part of the phosphoric acid was volatilized by the strong ignition necessary to convert the magnesium ammonium phosphate into the magnesium pyrophosphate. When large quantities of ammonium salts are present,  $\text{Mg}(\text{NH}_4)_2(\text{PO}_4)_2$  is precipitated as well as the normal  $\text{MgNH}_4\text{PO}_4$ . The former salt upon ignition reacts according to the following formula:



And upon continued ignition the metaphosphate is converted into the pyrophosphate with loss of phosphoric anhydride:



The amount of anhydride lost is proportional to the amount of  $\text{Mg}(\text{NH}_4)_2(\text{PO}_4)_2$  formed, which in turn is dependent upon the quantity of ammonium salts in solution.

Breyer and Schweitzer (*Chem. Ztg.*, 1892, 1720-23) question the accuracy of the Lindo-Gladding method for potassium. They claim that an examination of the potassium-platinic chloride precipitate showed the presence of sulphuric acid, lime, magnesia, and ammonia. As their results were low in comparison

with the Fresenius method in spite of these impurities they concluded there was a loss of potash in the determination, and tests of the alcoholic washings showed potash. A sample of sylvinite contained 15.45 per cent. potash by the Fresenius method and 14.85 per cent. potash by the Lindo-Gladding method. The platinum precipitate of the former was free from sulphuric acid, lime, magnesia, or ammonia. The ammonium chloride and alcoholic washings in the Lindo-Gladding method contained potash equivalent to 1.46 per cent. potash for 0.5 gram of substance. Analysis of the platinum precipitate showed ammonia equivalent to 0.0176 gram of ammonium-platinic chloride or in weight to 0.0034 grams potassium-platinic chloride or 0.68 per cent. potash for 0.5 gram of substance. Sulphuric acid and magnesia were also recognized qualitatively in the potassium-platinic chloride.

Holleman (*Chem. Ztg.*, 1892, 1920-21) explains the unsatisfactory results obtained by Breyer and Schweitzer in that, notwithstanding the large quantity of alcohol used for washing the precipitate, the soluble platinum salts were not all removed and consequently in the washing with ammonium chloride, ammonium-platinic chloride was formed which remained on the filter as an impurity. To this Holleman attributed the presence of ammonia in the platinum precipitate and not to a partial replacement of the potash of the platinum salt by ammonia in washing.

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## ALUMINUM.<sup>1</sup>

BY R. L. PACKARD,

ASIDE from the merely industrial aspect of the subject, the history of aluminum is unique in affording an opportunity to study the growth, absolutely *ab initio* and within the space of one generation of men, of a metallurgical industry operating upon a new metal. Thirty-five years ago aluminum was as much a chemical curiosity as any one of the rare metals is to-day. Through the efforts of Deville it first acquired a commercial character, and its extraction was transferred from the sphere of laboratory experiments to become a metallurgical process. Since

<sup>1</sup> From *Bulletin of the U. S. Geological Survey*, April, 1893.



his day the development of electro-metallurgy, largely due to the attempts to produce aluminum economically, has increased to such an extent that the chemical process founded by him has now given way to the electrical form of metallurgy in extracting the new metal. Following this change in metallurgy and the increase in its production, attention has been drawn to other materials as sources of the metal than the cryolite formerly used, and new occurrences of the ore of aluminum, which has now acquired an increased value, are sought for. This increase of commercial demand, in turn, has caused the new ore and its deposits to be studied and explained by the aid of the most recent scientific methods. From the technical and industrial point of view, we have now to deal with ores of aluminum as well as ores of iron. From the scientific standpoint, while much is known of the origin of iron ores, little special attention has yet been paid to the genesis of ores of aluminum on account of the recent appearance of the latter metal in the arts. This metal, however, has the advantage of making its debut in the full light of every known modern means of investigation—chemical, mineralogical, geological, and petrographical—and the scientific explanation of its origin will doubtless be speedy and full. To supplement the technology of the metal, it is deemed advisable to collect and introduce here what is at present known of its ores and their occurrence and origin.

In the census bulletin on aluminum, prepared under the supervision of this Division, it was stated that the aluminum produced in this country (by the Pittsburgh Reduction Company) was then (1889) mainly obtained from Greenland cryolite. No workable deposits of cryolite have been authentically reported in this country. The deposit at the southern base of Pike's Peak, Colorado, described by Messrs. Cross and Hillebrand, in Bulletin No. 20, of the U. S. Geological Survey, was shown by them to be only of mineralogical interest. Bauxite deposits and "alum beds" of considerable extent have, however, been found, and the former mineral is used as a source of aluminum. It is the ore of aluminum and occurs in Georgia, Alabama, and Arkansas.

The mineral received its name from Baux, a village in the

south of France, where it was first found, and the more highly ferriferous variety was regarded and worked as an iron ore, but proved too refractory. It sometimes ran as high as forty-two per cent. metallic iron. The analysis by Berthier revealed its true character. The geological occurrence of the bauxite of Baux was studied by H. Coquand (*Bull. Soc. Geolog. de France*, 28, 98, 1871), who describes the mineral as of three varieties, pisolitic, compact, and earthy. The pisolitic variety does not differ in structure from the iron ores of Franche Comté and Berry, although the color and composition are different. It occurs in highly tilted beds alternating with limestones, sandstones, and clays, belonging to the upper cretaceous period, and in pockets or cavities in the limestone. The limestone containing the bauxite and that adjacent thereto is also pisolitic, some nodules being as large as the fist, and the pisolitic bauxite has sometimes a calcareous cement, and at others is included in a paste of the compact mineral. M. Coquand supposed that the alumina and iron oxide composing the bauxite were brought to the ancient lake bed in which the lacustrine limestone was formed by mineral springs, which, discharging in the bottom of the lake, allowed the alumina and iron oxide to be distributed with the other sediment. In some cases the discharge occurred on land, and the deposit then formed isolated patches. He refers to other similar deposits of bauxite of the same period in France. Sometimes the highly ferriferous mineral predominates over the aluminous (white), at others diasporé is found enveloping the red mineral, while in other cases it is mixed with it, predominating largely, and sometimes manganese peroxide replaces ferric oxide. In some places the ground was strewn with fragments of tuberous menilite, very light and white.

M. Angé (*Bull. Soc. Geolog. de France*, 16, 345, 1888) describes the bauxite of Var and Hérault and gives analyses of it. Over 20,000 tons were being mined in this region annually at the time of writing his report (1888). In the red mineral of Var druses occur with white bauxite running as high as eighty-five per cent. alumina, and fifteen per cent. water, corresponding to the formula  $Al_2O_3 + H_2O$ . He refers to the prevailing theory of the formation of bauxite, according to which solutions of the

chlorides of aluminum and iron in contact with carbonate of lime undergo double decomposition, forming alumina, iron oxide, and calcium chloride. Other deposits in the south of France, in Ireland, Austria, and Italy, he says, confirm this view, because they also rest upon or are associated with limestone. The bauxite deposit in Puy de Dome which he studied, could not, however, be explained by this theory because it was not associated with limestone, but rested directly upon gneiss and was partly covered by basalt. The geological sketch map of the deposit near Madriat, Puy de Dome, which he gives, shows gneiss, basalt, with uncovered bauxite largely predominating, and patches of miocene clays, while the geological section of the deposit near Villeveyrac, Hérault, shows the bed of bauxite conformably following the flexures of the limestone formation when covered by more recent beds, and when exposed and denuded occupying cavities and pockets in the limestone. This occurrence is substantially the same as that of the neighboring Baux. M. Angé agrees with M. Coquand in attributing the bauxite to geysarian origin. He uses as an illustration of the contemporaneous formation of bauxite the deposits from the geysers of the Yellowstone Park, which is evidently due to a misunderstanding. He made no petrographical examination of the bauxite of Puy de Dome, nor did he attempt to trace any genetic relation between the latter and the accompanying basalt. The occurrence is, however, noteworthy, and an examination might show that it is another instance of the direct derivation of bauxite from basalt, which is maintained in the two following instances, somewhat imperfectly in the first to be sure, but with greater detail in the second.

The first is a paper by Lang in the *Ber. d. chem. Ges.*, **17**, 2892, 1884. He describes the bauxite in Ober-Hessen, which is found in the fields in round masses up to the size of a man's head, embedded in a clay which is colored with iron oxide. The composition varies very widely. The petrographical examination showed silica, iron oxide, magnetite, and augite. The chemical composition and petrographical examination shows the bauxite to be a decomposition product of basalt. By the weathering of the plagioclase feldspars, augite, and olivine, nearly all the silica

had been removed, together with the greater part of the lime and magnesia; the iron had been oxidized and hydroxid of alumina formed as shown by its easy solubility in hydrochloric acid. The residue of the silica had crystallized as quartz in the pores of the mineral.

The more detailed account of the derivation of bauxite from basalt is given in an inaugural dissertation by A. Liebreich, abstracted in the *Chem. Centrbl.*, 1892, No. 3, p. 94. This writer says that the well-known localities of bauxite in Germany are the southern slope of the Westerwald near Mühlbach, Hadamar, in the neighborhood of Lesser Steinheim, near Hanau, and especially the western slope of the Vogelsberg. Chemical analyses show certain differences in the composition of bauxite from different places, the smaller amount of water in the French bauxite referring it to diasporite, while the Vogelsberg mineral is probably Gibbsite (hydrargillite). The bauxites of Ireland, of the Westerwald, and the Vogelsberg, show by certain external indications their derivation from basalt. The bauxite of the Vogelsberg occurs in scattered lumps or small masses, partly on the surface and partly imbedded in a grayish white to reddish brown clay, which contains also similar masses of basaltic iron ore and fragments of more or less weathered basalt itself. Although the latter was associated intimately with the bauxite, a direct and close connection of the two could not be found, but an examination of thin sections of the Vogelsberg bauxite showed that most specimens still possessed a basaltic (anamesite) structure, which enabled the author to determine the former constituents with more or less certainty. The clays from different points in the district carrying basalt, basaltic iron ore, and bauxite were examined, some of which showed clearly a sedimentary character. Some of the bauxite nodules were a foot and a half in diameter and possessed no characteristic form. They were of an uneven surface, light to dark brown, white, yellowish, and gray in color, speckled and pitted, sometimes finely porous and full of small colorless or yellowish crystals of hydrargillite. The thin sections showed distinct medium-granular anamesitic structure. Lath-shaped portions filled with a yellowish substance preponderated (the former plagioclases) and

filling the spaces between these were cloudy, yellow, brown, and black transparent masses which had evidently taken the place of the former augite. Laths and plates of titanite iron, often fractured, were commonly present and the contours of altered olivine could be clearly made out. The anamesitic basalt of the neighborhood showed a structure fully corresponding with the bauxite. Olivine and titanite iron oxide were found in the clay by washing. The basaltic iron ore also showed the anamesite structure.

The American occurrences of bauxite so far observed are in Alabama, Georgia, and Arkansas. Prof. Eugene A. Smith, State Geologist of Alabama, has kindly furnished the following information in regard to the bauxite of that State. He writes:

"The mining of bauxite was begun in Alabama in November, 1891, by the Southern Bauxite Mining and Manufacturing Company, of Piedmont Alabama, which has shipped up to date (November, 1892) about 3,600 tons. In July, 1892, the Republic Mining and Manufacturing Company, of Hermitage, Georgia (which is the pioneer in the business), secured a lease of the mines of the Bass Furnace Company, at Rock Run, Cherokee county, and has shipped up to date, about 1,300 tons. In addition to this both companies have several hundred tons under sheds drying out. The ore goes to Philadelphia and Natrona, Pennsylvania; Syracuse, Buffalo, Brooklyn, New York, and other places. \* \* \* It comes into competition with the ore from Baux, in France, which can be purchased at a lower price than that at which this region can furnish it; but it is claimed by the manufacturers that our ore is more soluble, and therefore more valuable, though containing slightly less alumina. \* \* \* [Our] alumina runs from fifty-six per cent. to sixty per cent. average carload analysis. Of the insoluble matter silica is the chief ingredient. The ore contains from two to three per cent. of titanite acid, and will average from twenty-five per cent. to thirty per cent. of water. The ore occurs associated with limonites and kaolins in irregular beds, in the region underlain by the Knox dolomite of the Lower Silurian formation. In Alabama these occurrences are always near to the foothills of the mountains formed of the Weisner quartzite or sandstone, which is a member of the Cam-

brian in this State. The bauxite therefore seems to be associated chiefly with the lower beds of the Knox dolomite. The best known occurrences are near Rock Run furnace in Cherokee county, where it has been followed for a few miles towards the Georgia line. This is the only place in Alabama where any systematic mining is done, and this by the two companies above named whose mines are closely contiguous. Near Jacksonville, Alabama, in Calhoun county, the ore has also been discovered, but not yet mined commercially.

“The mines are in S. twenty-five, T. eleven, R. eleven, about three and one-half miles northeast of Rock Run furnace and close to the Georgia line. In mining the limonite in one place great quantities of bauxite were moved and lie now in the dump pile. This was before it was recognized as bauxite.”

The statistical information in the foregoing was furnished to Prof. Eugene A. Smith, State Geologist of Alabama, by Mr. J. M. Garvin, superintendent of the Rock Run Furnace Company.

He sends analyses, which are included with the others on a subsequent page.

The Georgia bauxite occurs in the same formation. The Bureau is indebted to Mr. J. W. Spencer, State Geologist of Georgia, for the following account of its occurrences:

“It occurs in the residual clay from decomposition of the Knox (calciferous) dolomite formation, which series is greatly developed in Georgia. The principal belt commences near Adairsville and widens out, extending in a southwest direction to Alabama. It occurs in the vicinity of brown iron and manganese ores. Indeed, the bauxite-bearing portion of the Knox series is nearly coincident with the manganese deposits. It occurs in pockets, often of great extent, and is usually covered with a few feet of clayey surface. A kaolin is often associated with it. It is mostly in concretionary nodules forming large masses or small kidney-shaped masses scattered through the clay. Much of the bauxite is light colored, but other portions contain much iron. At one locality Gibbsite occurs associated with it. It evidently has a similar origin with the brown iron or manganese ores, and was probably deposited in lagoons from solution of decomposed crystalline rocks, which occur eighteen

or twenty miles to the east. Alumina is slightly soluble in water containing  $\text{CO}_2$ , as are also the other metals." The analyses of the Georgia bauxite by Prof. H. C. White are given below.

An estimate of the quantity of bauxite mined in Georgia, furnished to this division by Mr. Wm. G. Neilson, of Philadelphia, gives 728 tons for 1889, 1,850 tons for 1890, and 3,300 for 1891. The total output for Alabama up to June, 1892, was 3,200 tons.

The Arkansas bauxites occur in Tertiary areas and in the neighborhood of eruptive syenites, to which they seem to be genetically related. The mineral is pisolitic in structure, and varies in color and chemical composition (analysis below). It has been mined for iron ore, some specimens yielding fifty per cent. metallic iron, and is of great abundance (Prof. J. C. Branner, *American Geologist*, 7, 181).

Having now traced the ore of aluminum to its origin, as far as present information will allow, the following analyses will show the wide variations in its composition :

*Analyses of bauxite, from Baux :*

[ANALYST, DEVILLE.]

	Compact variety. Per cent.	Pisiform. Per cent.	Hard and compact calcareous paste. Per cent.	Bauxite from Calabres. Per cent.
$\text{SiO}_2$ .....	2.8	4.8	...	2.0
$\text{Al}_2\text{O}_3$ .....	57.6	55.4	30.3	33.2
$\text{Fe}_2\text{O}_3$ .....	25.3	24.8	34.9	48.8
$\text{H}_2\text{O}$ .....	10.8	11.6	22.1	8.6
$\text{TiO}_2$ .....	3.1	3.2	...	1.6
$\text{CaCO}_3$ .....	0.4	0.2	12.7	...
Corundum.....	...	...	...	5.8
Total.....	100.0	100.0	100.0	100.0

*French bauxites of two different types :*

	Red baux- ite from Thoronet, Var. Per cent.	White bauxite from Ville- veyvae Hérault. Per cent.
$\text{SiO}_2$ .....	0.30	2.20
$\text{Al}_2\text{O}_3$ .....	69.30	76.90
$\text{Fe}_2\text{O}_3$ and $\text{FeO}$ .....	22.90	0.10
$\text{H}_2\text{O}$ .....	14.10	15.80
$\text{TiO}_2$ .....	3.40	4.00
Total.....	110.00	99.00

*Analyses of German bauxite :*

## FROM WOCHEIN.

[ANALYST, LILL.]

SiO <sub>2</sub> .....	6.29	per cent.
Al <sub>2</sub> O <sub>3</sub> .....	64.24	" "
Fe <sub>2</sub> O <sub>3</sub> .....	2.40	" "
CaO .....	0.85	" "
MgO .....	0.38	" "
SO <sub>3</sub> .....	0.20	" "
P <sub>2</sub> O <sub>5</sub> .....	0.46	" "
H <sub>2</sub> O .....	25.74	" "
Total .....	100.56	" "

## FROM LANGSDORF.

[ANALYST, LANG.]

	Brownish red. Per cent.	Light red. Per cent.
SiO <sub>2</sub> .....	5.14	10.27
Al <sub>2</sub> O <sub>3</sub> .....	50.85	49.02
Fe <sub>2</sub> O <sub>3</sub> .....	14.36	12.90
FeO .....	0.35	not det.
CaO .....	0.41	0.62
MgO .....	0.11	trace
K <sub>2</sub> O .....	0.09	0.11
Na <sub>2</sub> O .....	0.17	0.20
H <sub>2</sub> O (ign.) .....	27.03	25.88
H <sub>2</sub> O (100°) .....	1.35	0.93
CO <sub>2</sub> .....	trace.	0.26
P <sub>2</sub> O <sub>5</sub> .....	0.48	0.38
Total .....	100.34	100.57

## FROM VOGELSBERG.

[ANALYST, LIEBREICH.]

SiO <sub>2</sub> .....	1.10	per cent.
Al <sub>2</sub> O <sub>3</sub> .....	50.92	" "
Fe <sub>2</sub> O <sub>3</sub> .....	15.70	" "
CaO .....	0.80	" "
MgO .....	0.16	" "
H <sub>2</sub> O (ign.) .....	27.75	" "
H <sub>2</sub> O (100°) .....	0.85	" "
TiO <sub>2</sub> .....	3.20	" "
Total .....	100.48	" "

*Analyses of Alabama bauxite :*

[ANALYST, DR. WM. B. PHILLIPS.]

	From Cherokee county. Per cent.	Jackson- ville, Calhoun county. Per cent.	Jackson- ville, Calhoun county, red. Per cent.	Jackson- ville, Calhoun county, white. Per cent.
SiO <sub>2</sub> .....	37.87	18.67	7.73	23.72
Al <sub>2</sub> O <sub>3</sub> .....	39.44	45.94	47.52	41.38
Fe <sub>2</sub> O <sub>3</sub> .....	2.27	11.86	19.95	0.85
H <sub>2</sub> O hygroscopic	9.20	1.40	23.57	23.72
H <sub>2</sub> O combined	12.80	21.20		
TiO <sub>2</sub> .....	....	....	....	....



or twenty miles to the east. Alumina is slightly soluble in water containing  $\text{CO}_2$ , as are also the other metals." The analyses of the Georgia bauxite by Prof. H. C. White are given below.

An estimate of the quantity of bauxite mined in Georgia, furnished to this division by Mr. Wm. G. Neilson, of Philadelphia, gives 728 tons for 1889, 1,850 tons for 1890, and 3,300 for 1891. The total output for Alabama up to June, 1892, was 3,200 tons.

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$\text{SiO}_2$ .....	0.30	2.20
$\text{Al}_2\text{O}_3$ .....	69.30	76.90
$\text{Fe}_2\text{O}_3$ and $\text{FeO}$ .....	22.90	0.10
$\text{H}_2\text{O}$ .....	14.10	15.80
$\text{TiO}_2$ .....	3.40	4.00
Total .....	110.00	99.00

	Per cent.	Per cent.	Per cent.
SiO <sub>2</sub> .....	2.00	10.38	16.76
Al <sub>2</sub> O <sub>3</sub> .....	62.05	55.64	51.90
Fe <sub>2</sub> O <sub>3</sub> .....	1.66	1.95	3.16
TiO <sub>2</sub> .....	3.50	3.50	3.50
H <sub>2</sub> O (ign.).....	30.31	27.62	24.86
Total .....	99.52	99.09	100.28

*Metallurgy.*—The electrolytic process by which aluminum is extracted from its oxide, alumina, is now well understood by all persons interested in the subject. In this country it is carried on by the Pittsburgh Reduction Company. The principle is that alumina is decomposed in the presence of a melted fluoride by the electric current, and metallic aluminum is liberated. Powerful dynamos furnish the current for this purpose. In practice the alumina is dissolved in the fused flux, consisting of fluorides of aluminum and sodium, which is regarded as serving as a vehicle for the alumina. The furnace for effecting the operation is made in the form of an open iron-cased box which is thickly lined with carbon and is provided with a spout at the bottom for tapping off the aluminum. A large block, or series of bars of carbon, carried on an adjustable support and arranged to dip into the center of the furnace, forms the anode, the furnace itself forming the cathode. After the flux and alumina have been introduced the carbon anode is brought well down into the furnace and the current turned on. At first considerable resistance is offered, but as the materials in the furnace become highly heated this decreases, and the anode can be raised somewhat. Decomposition soon begins, the alumina being resolved into oxygen and metallic aluminum, the former being liberated at the anode, and, combining with the carbon of which it is composed, passes off as carbonic oxide, while the metallic aluminum, being heavier than the melted bath, sinks to the bottom of the latter and is tapped off from time to time. As the alumina is used up the increase in resistance indicates the progress of the reduction, and fresh alumina is added. The operation is therefore continuous.

Several new processes were patented during the year 1891 in Europe and in this country, the published character of which describe variations (improvements) on those already well known.

*Analyses of bauxite from Jacksonville, Calhoun county, Alabama :*

[ANALYST, W. F. HILLEBRAND.]

	Red. Per cent.	White. Per cent.
SiO <sub>2</sub> .....	10.25	21.08
Al <sub>2</sub> O <sub>3</sub> .....	41.00	48.92
Fe <sub>2</sub> O <sub>3</sub> .....	25.25	2.14
TiO <sub>2</sub> .....	2.53	2.52
P <sub>2</sub> O <sub>5</sub> .....	trace	trace
H <sub>2</sub> O (100°) .....	0.65	0.45
H <sub>2</sub> O (ign.).....	20.43	23.41
Total .....	100.11	98.62

CaO, MgO, and alkalis, not looked for.

*Analyses of bauxite from Floyd county, Georgia :*

[ANALYST, NICHOLS.]

	Per cent.	Per cent.	Per cent.
SiO <sub>2</sub> .....	2.80	....	2.30
Al <sub>2</sub> O <sub>3</sub> .....	52.21	57.25	56.88
Fe <sub>2</sub> O <sub>3</sub> .....	13.50	3.21	1.49
TiO <sub>2</sub> .....	3.52	3.60	3.55
H <sub>2</sub> O .....	27.72	....	....
P <sub>2</sub> O <sub>5</sub> .....	....	....	0.07
Total .....	99.75	....	....

*Other analyses of bauxite from Georgia :*

[ANALYST, PROF. H. C. WHITE.]

	1 Per cent.	2 Per cent.	3 Per cent.	4 Per cent.	5 Per cent.	6 Per cent.	7 Per cent.
SiO <sub>2</sub> .....	19.56	41.47	2.56	8.29	6.62	35.88	1.98
Al <sub>2</sub> O <sub>3</sub> .....	52.13	39.75	56.10	58.61	59.82	45.21	61.25
Fe <sub>2</sub> O <sub>3</sub> .....	1.12	1.62	10.64	2.63	2.16	0.52	1.82
H <sub>2</sub> O .....	24.21	16.14	30.10	27.42	31.10	17.13	31.43
TiO <sub>2</sub> .....	2.08	....	....	3.15	....	....	2.38
Total ..	99.10	98.98	99.30	100.10	99.70	98.74	98.86

Number seven is on the Barnsley estate, Dinwood Station. It is a large deposit and is being now largely opened for working. It always contains titanitic acid and usually traces of alkalis, etc.

*Bauxite from Pulaski county, Arkansas :*

	Black.			Red.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
SiO <sub>2</sub> .....	10.13	11.48	5.11	4.89	3.34
Al <sub>2</sub> O <sub>3</sub> .....	55.59	57.62	55.89	46.40	58.60
Fe <sub>2</sub> O <sub>3</sub> .....	6.08	1.83	19.45	22.15	9.11
H <sub>2</sub> O .....	28.99	28.63	17.39	26.68	28.63
Total..	100.79	99.56	97.84	100.12	99.68

	Per cent.	Per cent.	Per cent.
SiO <sub>2</sub> .....	2.00	10.38	16.76
Al <sub>2</sub> O <sub>3</sub> .....	62.05	55.64	51.90
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weight. The results, which fill a large table, showed that in most cases there was absolutely no action and in the few cases where there was a perceptible loss of weight it was so trifling as to be disregarded. To the objection that continued drinking of fluids containing a small quantity of alumina would eventually be dangerous, the author points out that the ash of all the fluids usually drank contains alumina, as well as most foods and drinking water itself. His conclusion is that there is no objection to the use of aluminum for canteens and similar vessels.

These conclusions of Rupp were confirmed by Dr. A. Arche (*Dingler's poly. J.*, **284**, No. 11, 255), whose experiments show that the purity of aluminum (using the percentage of silicon as a means of classification) has much to do with its power of resisting the solvent action of fluids, and they also show that the mechanical preparation of the metal is an important factor. He found that hammered aluminum was least attacked, rolled metal came next, and then the drawn metal, while cast metal was much more easily attacked (by acetic acid).

(To be continued.)

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WILLIS.

*Iron and Steel.*—Finely powdered wood charcoal with animal charcoal is a combination given by H. A. Harvey for supercarburizing steel (408,300). John A. Hunter has three patents: 498,061 is a process for increasing the per cent. of carbon in low steel by subjecting molten metal in a suitable converter to the action of a blast composed of the gases resulting from heating together hydrochloric acid, calcium chloride, carbon, and sodium chloride; 498,062 is a method for converting iron into steel by heating in a crucible or retort, subjecting to action of a gas containing chlorine, oxygen, and hydrogen evolved from hydrochloric acid, calcium chloride, and sodium chloride; 498,063 is another patent on a process for increasing the per cent. of carbon in steel by subjecting the red hot metal in a crucible or retort to the action of chlorine and oxygen, which have first been brought into contact with heated carbon. To concentrate and separate ores, John W. Meier heats and converts into ferric oxide, then into magnetic oxide by heating with carbonaceous substance, and reducing gases as carbon dioxide and then separates with the magnet 497,894.

*Sulphur and Carbon Disulphide.*—A process for roasting sulphur bearing ores and obtaining sulphur in the solid form, Charles W. Stickney, inventor, consists in roasting one portion by means of steam and

According to these results almost pure aluminum, 99.5 per cent., is attacked even in the cold by nitric and sulphuric acids, so that the metal should not be used in apparatus for preparing these acids.

As to the action of drinking fluids, coffee, tea, beer, wines, brandy, etc., the following appears to be the state of the case: Messrs. Lübbert and Roscher (*Chem. Centrbl.*, 1891, 11, No. 18, 780) tested the resistance of aluminum to the action of alcohol, ether, aldehyde, coffee, tea, wines, and antiseptics, by allowing aluminum leaf to remain in concentrated solutions of the different liquids four days at the temperature of the room, and the fluids were examined either directly for alumina or were evaporated and the ignited residue so examined. The conclusion reached was that aluminum possesses only a slight degree of resistance to the agents named, except alcohol, ether, and aldehyde, and that it is therefore unsuitable for wares which are to be used for acid drinks, coffee, tea, etc., or articles which are to be cleaned with soda or soap. Its application in daily life would therefore be very limited.

On the other hand, G. Rupp (*Dingler's poly. J.*, 283, No. 1, January 21, 1892), criticises the methods employed by Lübbert and Roscher for determining the action of the fluids by estimating the alumina contained in them, as well as the use of aluminum leaf for their experiments, which is attacked much more easily than the compact metal, the former being acted on even by boiling water, while the latter is unaffected. His own experiments were made upon aluminum vessels (canteens, drinking cups, etc.), and foil, the object being to determine the availability of the metal for use in the army. The carefully dried and weighed vessels were filled with the different fluids or the foil was immersed in them, and the action was allowed to continue four, eight, and twenty-eight days, at the temperature of the room with frequent stirring. The fluids included wines of different kinds, beer, kirschwasser, cognac, coffee, tea, milk, drinking water, one per cent. solution of tartaric acid, acetic acid (one per cent., four per cent., ten per cent., solutions), vinegar (ten per cent.), soda solution (one per cent.), besides butter, honey, and preserved fruits. The articles were then cleaned, dried, and weighed, to determine the loss of

weight. The results, which fill a large table, showed that in most cases there was absolutely no action and in the few cases where there was a perceptible loss of weight it was so trifling as to be disregarded. To the objection that continued drinking of fluids containing a small quantity of alumina would eventually be dangerous, the author points out that the ash of all the fluids usually drank contains alumina, as well as most foods and drinking water itself. His conclusion is that there is no objection to the use of aluminum for canteens and similar vessels.

These conclusions of Rupp were confirmed by Dr. A. Arche (*Dingler's poly. J.*, **284**, No. 11, 255), whose experiments show that the purity of aluminum (using the percentage of silicon as a means of classification) has much to do with its power of resisting the solvent action of fluids, and they also show that the mechanical preparation of the metal is an important factor. He found that hammered aluminum was least attacked, rolled metal came next, and then the drawn metal, while cast metal was much more easily attacked (by acetic acid).

(To be continued.)

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## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Iron and Steel.*—Finely powdered wood charcoal with animal charcoal is a combination given by H. A. Harvey for supercarburizing steel (498,390). John A. Hunter has three patents: 498,061 is a process for increasing the per cent. of carbon in low steel by subjecting molten metal in a suitable converter to the action of a blast composed of the gases resulting from heating together hydrochloric acid, calcium chloride, carbon, and sodium chloride; 498,062 is a method for converting iron into steel by heating in a crucible or retort, subjecting to action of a gas containing chlorine, oxygen, and hydrogen evolved from hydrochloric acid, calcium chloride, and sodium chloride; 498,063 is another patent on a process for increasing the per cent. of carbon in steel by subjecting the red hot metal in a crucible or retort to the action of chlorine and oxygen, which have first been brought into contact with heated carbon. To concentrate and separate ores, John W. Meier heats and converts into ferric oxide, then into magnetic oxide by heating with carbonaceous substance, and reducing gases as carbon dioxide and then separates with the magnet (497,804).

*Sulphur and Carbon Disulphide.*—A process for roasting sulphur bearing ores and obtaining sulphur in the solid form, Charles W. Stickney, inventor, consists in roasting one portion by means of steam and

mechanical agitation, generating hydrogen sulphide, and roasting another portion by means of air, generating sulphur dioxide, and mingling these gases in contact with a solution of a sulphate of a heavy metal (493,193). Martin Wanner proposes to manufacture carbon disulphide from reduced sulphide ores by mixing the finely divided reduced sulphide with powdered carbon, then moistening the mass with liquid hydrocarbon, heating in a closed retort, condensing the carbon disulphide, and removing reduced metal from furnace (497,256).

*Alkali Recovery, etc.*—An apparatus for recovering alkali (497,088) belongs to Henry Blackman, and Thomas Craney claims 496,863, an apparatus for the electrolysis of salt, and 496,866, an arrangement for washing salt. M. M. Monsanto has an improved process for manufacturing salt (496,615). John A. Just decomposes the manganese dioxide and chloride left after the evolution of chlorine, with nitric acid, removes the manganous nitrate to a neutralizing well, adds manganese protoxide, hydrate, or carbonate, transfers to a settling tank, then to a concentrator worked by waste heat, next to calcining furnaces to decompose, condensing evolved gases and recovering the nitric acid (495,462). W. T. Gibbs and S. P. Franchot (493,023) patent their process for obtaining chlorates of the alkalis or the alkaline earths by electrolysis, while O. Lugo (493,277) deposits metals from a liquid paste composed of a mixture of the insoluble salts of the metals with water by passing the electric current. Karl Sundstrom (492,929) has an improvement in the manufacture of soda. Bicarbonate mud is first purified by dissolving out the ammonia compounds with a suitable solvent, then passing water in a finely divided spray to remove the sodium chloride.

*Sugar, etc.*—Eugen Langen has a patent process for refining sugar (495,614), and Dr. Fahlberg takes out two patents on his improved process for manufacturing pure saccharine, 496,112 and 496,113. A dry mixture of para sulphaminbenzoic acid and ortho sulphaminbenzoic acid is added to an aqueous solution of an alkali or alkaline earth containing just enough alkali to neutralize and dissolve only the ortho acid, filtering off the liquid from the undissolved para acid, and adding to the filtrate an acid stronger than the ortho sulphaminbenzoic acid, whereby the saccharine is precipitated. Alfred Wohl and Alexander Kollrepp (498,000) mix saccharine solutions containing sixty per cent. or more of sugar with dilute acid, heat the mixture and neutralize the acid to obtain invert sugar. Georges de Laire has a process for manufacturing vanilloyl-carbonic acid and vanilline (497,546).

*Tanning, Bleaching, and Dyeing.*—495,028 covers a process for tanning leather, granted Martin Dennis. After treatment in a bath of basic chloride of chromium to fix the gelatine, the hides are subjected to a bath of suspended carbonate of calcium. Heinrich Thies and Emil Herzig dip articles to be bleached first in hydrofluoric acid solution, then steam and wash in a bath containing an alkaline earth compound, again steam and treat with boiling caustic alkali lye (496,072). Peter T. Austen



- obtains a solid extract of sumac, hemlock, etc., by incorporating an alkaline nitrite (495,768). Fritz Bender patents a blue dye derived from dimethyl metamido-cresol and derivatives of aromatic amines (494,838) and R. E. Schmidt and Paul Tust obtain an alizarine dye by oxidizing beta nitro-anthropurine with manganese dioxide in sulphuric acid solution (496,139).

*Miscellaneous.*—Wm. W. Jacques uses grains of carbon treated with alumina for granulated material for transmitting telephones (495,090). Jonas E. Blomén dissolves picric acid and a hydrocarbon separately, then mixes, and the "picrated" hydrocarbon is dissolved in nitroglycerol, forming a blasting compound (495,178). Robert Hutchinson has a composition for lubricant, lime combined with fatty acids in excess, with a mineral or hydrocarbon oil and an alkali "pinate" (496,225). Paper pulp, sour milk, albumen, lime, and chloride of zinc form the combination which Wm. P. Emery proposes to use for making railroad ties (495,581). To make coal-briquettes, John N. Macrath adds to coal-dust a binder of a viscous liquid (made by boiling wood moss in silicic acid) and a solution of silicic acid (495,679). R. J. Parke and Isaac Goodman have a paint-filling composition (496,277) and "soap, ether, ammonia, glycerol, alcohol, and water" form a cleaning compound patented by Charlotte E. Moor (496,274). Otto Jensen and R. Keck claim the rock "phonolite," sodium sulphate, and limestone as a glass composition (494,636). Another patent wall-plaster, Barbara Dirnberger, the inventor, consisting of sand, plaster of Paris, slaked lime, muriatic acid, lime, soluble glass, glue water, and tissues of fiber (494,981.) Frank S. Culver has two patents on a fire-proofing composition, 495,149 and 495,166, the former containing a large proportion of asbestos fiber, plaster of Paris, and a small proportion of gypsum cement with a binding fiber of jute or hemp, while the latter patent omits the gypsum. Herman Giessler mentions pulverized magnetic oxide of iron, a metallic soap, a glass flux, and a refractory body-substance as emery or metallic powder, as a compound for coating metallic surfaces with a film of vitreous luster and dark violet blue color (495,629). A compound of cresol—para-isobutyl-ortho-cresol iodide—a yellow powder, soluble in ether, chloroform, and olive oil, which decomposes above 60° C., and on further heating gives off iodine vapors, is patented by Josef Messinger and G. Vortmann (495,204). Louis Aronson (497,621) for an electro-tinning bath uses a combination of water, ammoniacal alum, chloride of tin, sodium pyrophosphate and caustic soda. T. S. Harrison and C. Semper have two patents: one (497,570) an "aluminous compound," composed of sulphate of aluminum, and a double sulphate of aluminum and soda; and the other (497,571) an improvement in the process for making same, which consists in hardening or drying by the addition of sulphate of soda. M. L. Griffin (497,785) precipitates calcium carbonate by adding lime to a soluble carbonate, then mixes the precipitate with clay, dries, calcines, and grinds to form Portland cement. George Wegner and Paul Gührs

prepare articles to be electroplated with aluminum by first steeping in a bath of "acetic verdigris dissolved in vinegar," oxide of iron, sulphur, and ammonium chloride, brushing after removal from bath with a soft brass wire brush and rinsing with water (496,176). F. J. Clamer's method for coating metal articles, is first to clean by making them anodes in an electrolytic cell, then washing in a bath of dilute hydrochloric acid, immersing next in a bath of molten lead and phosphorus, and finally subjecting to pressure (494,667 and 668). To prepare basic bismuth gallate, which is described as a yellow powder, odorless, insoluble in water, dilute acids, alcohol and ether, but soluble in a large excess of mineral acids and containing 55-56 per cent.  $\text{Bi}_2\text{O}_3$ , Arthur Liebricht uses the method following: Neutral bismuth nitrate is dissolved in dilute nitric acid, a solution of gallic acid, alcohol, and water is added, and to this mixture caustic alkali or alkali carbonate until just slightly acid, when the salt is precipitated either with sodium acetate or by diluting with water (495,497). Emil Jacobsen forms sulfur compounds of hydrocarbons, according to his patent, 495,343, and Adolf Spiegel describes his method of obtaining sulpho-compounds in 495,124. Hydrocarbons are treated first with caustic soda, then with sulphuric acid, washed with water and brine successively, and the washed product is neutralized with alkali and the sulpho products separated by some suitable solvent. Leonard Paget has five patents, the first and second, 494,790 and 495,263, on pyroxyline solvents, the other three on pyroxyline compounds—494,791, 494,792, 494,793. Dieudonné Rigole extracts gutta percha from the leaves and twigs of the gutta percha tree, according to 495,757. To preserve meat, F. G. Dosmond and Jean F. Rozès exhaust air from the receptacle, and introduce under pressure gases obtained by calcining charcoal which has absorbed water (496,047). Peter Murray uses the following scheme to preserve timber: After coating with coal oil or mineral oil, animal fat, and brimstone, he burns the composition while applied to the timber until the composition is consumed (495,991). Samuel P. Sadtler and John H. Grimm patent a process for obtaining licorice extract (495,271) and Alfred Dervaux purifies water by charging an upwardly flowing column with lime at a point below the outlet of the water, forcing the lime to gravitate against the water and decanting the charged water at a safe distance below (495,313). H. L. Castner manufactures the higher oxides of sodium and potassium from the alkali metals by heating to  $300^\circ\text{C}$  and oxidizing the metals by the action of air with a decreasing proportion of nitrogen (494,757). James J. Fronheiser mixes an aqueous solution of iron sulphate and sulphuric acid, evaporates, and adds finely divided ferruginous matter and heats in his process for pigments (495,197). To convert insoluble hydrated phosphates of alumina into soluble forms, Stephen L. Goodale heats the hydrates in suitable receptacles until the water of combination is expelled and then allows the phosphates to cool spontaneously (493,889).

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## NOTES.

*The Chemical Congress at Chicago.*—Dr. Wm. McMurtrie sends the following additional information :

It has been arranged that during the progress of the meeting of the World's Congress of Chemists, two afternoon sessions will be devoted to and be spent among the exhibits of chemical products of the World's fair under the guidance and auspices of the exhibitors of those products. Most of these exhibits are worthy of the most careful study and these afternoon meetings are therefore sure to be both pleasant and profitable.

H. W. Wiley, F. W. Clarke, and J. H. Long have been made a committee on program. A number of titles of papers have been received and there will be a full week of work. I have received the following in addition to those received by Dr. Wiley, the titles of which have been published :

Prof. C. E. Munroe, Washington, "The Fulminates; their Preparation and Uses;" Prof. C. E. Munroe, "The Commercial Preparation of Calcium Phosphide;" Dr. Geo. Lunge, Zurich, "On Apparatus for the Interaction of Liquids and Gases;" Dr. Geo. Lunge, "The Education of Industrial Chemists;" Dr. Chas. A. Doremus, New York, "On Purification of Water;" Chas. A. Serre, B. Sc., F. C. S., New York, "On the Manufacture of Essential Oils;" Prof. S. P. Sadtler, Philadelphia, "On Recent Developments in Mineral Tanning in the U. S.;" Louis Jos. Mátyos, M. E., "Some Chemical and Mechanical Considerations Involved in the Scouring of Animal Fibers;" F. P. Vandenberg, Buffalo, "Asphalt, its Occurrence, Composition, and Technology;" Dr. G. B. Frankforter, Lincoln, Neb., "The New Formula for Narceine and its Alkali and Ethereal Salts;" Dr. G. B. Frankforter, "The Analogy Existing between Narcoline and Narceine."

The number of chemists who have expressed an intention to attend the meetings of the Congress and of the American Chemical Society is constantly increasing and a very large gathering is promised.

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## ERRATUM.

In the article entitled, "The Electrolytic Separation of the Metals of the Second Group," page 198, fourth line from the top, "five minutes" should read "five hours."

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### LEWIS MILLS NORTON, PH.D.

**D**R. LEWIS MILLS NORTON, a member of the Council of the American Chemical Society, died after a short illness on April 26, 1893. He was born in Athol, Mass., and was the only son of the Rev. John Foote Norton and Ann Maria Mann. His early youth was spent in Athol, Wellesley, and Natick, Mass., and in Fitz William and Keene, N. H.

He was an earnest student of chemistry at the Institute of Technology for three years, from 1872 to 1875, when he was appointed assistant in analytical chemistry, in which capacity he served for two years. In May, 1877, he went to Europe and continued his chemical studies at Berlin, Paris, and Göttingen until August, 1879, and received his degree of Doctor of Philosophy from the University of Göttingen.

On his return to this country he entered the Amoskeag Manufacturing Company, of Manchester, N. H., as chemist, where he gained valuable practical experience which strongly influenced his subsequent career as a teacher of industrial chemistry.

In 1881 he returned to the Massachusetts Institute of Technology as instructor in general chemistry. In 1883 he was appointed assistant professor in organic chemistry, and in 1885 associate professor in organic and industrial chemistry. The combined duties of these two growing departments proved to be too much for one man to carry, and Dr. Norton gave up the systematic instruction in organic chemistry at the end of the Institute year in 1891, and after that time devoted his entire thought and strength to the subject of industrial chemistry, in which he was deeply interested.

In 1888 the faculty of the Institute of Technology, upon the scheme presented by Dr. Norton, founded the course in chemical engineering. That a course of study was needed which should add to a thorough training in mechanical engineering a fair knowledge of general, theoretical, and applied chemistry, was at once evident from the number of students of fine scholarship who entered the new course. Under Dr. Norton's fostering care the course in chemical engineering increased in numbers and efficiency. He gave it his best thought and effort, and happily saw before his death the course established on a firm foundation.

The kind of work for which the students are fitted in the course in chemical engineering at the Institute of Technology may be seen in the titles of the students' thesis work, which was superintended by Dr. Norton. In many cases, as will be seen in the list which follows, the investigations necessitated on the part of the student a knowledge both of the principles of chemistry and of mechanical engineering.

The Commercial Production of Oxygen by Electrolysis.

A Study of the Effect of a Live Steam Feed-Water Purifier on the Composition of the Feed-Water.

On the Production of Chlorine and Sodium Hydrate by the Electrolysis of Common Salt.

On the Heat of Vaporization of Ammonia.

Experiments upon the Relative Effect of Burners for Fuel and Illuminating Gases.

An Experimental Investigation of the Bisulphite Process of Making Chemical Fiber.

The Conditions of Maximum and Minimum Sulphuric Anhydride Formation in Burning of Sulphur.

The Explosion of Kerosene Lamps.

Experiments with Alloys Suitable for Digesters Used in Making Chemical Fiber by the Bisulphite Process.

On the Effect of the Aniline Black Process upon the Strength of Cotton Fiber.

An Investigation of the Efficiency of a Mechanical Stoker.

The Electrolytic Deposition of Nickel.

An Investigation into the Amount of Heat Lost in the Flue Gases from Steam Boilers.

An Investigation of the Specific Heat of Brines.

The professional papers contributed by Dr. Norton to various scientific and technical journals were very numerous, and in-

cluded a wide range of subjects. The following list includes his more important papers :

1878. (With A. Michael.) Ueber die Einwirkung des Chlorjods auf Aromatische Amine. *Ber. d. chem. Ges.*, 1878, 107.
1879. Ueber die Einwirkung von Chlorjod auf die Amine der Benzolreihe. Inaugural Dissertation. Pph., 8vo, pp. 36. Göttingen.
1879. (With A. Michael.) On the Action of Iodine Monochloride upon Aromatic Amines. *Am. Chem. J.*, 1, 255-267.
1880. (With same.) On Alpha—and—Beta Monobromcrotonic Acids. *Id.*, 2, 11-19.
1884. (With C.O.Prescott.) Continuous Etherification. *Id.*, 6, 241-246.
1884. (With W. R. Nichols.) Laboratory Experiments in General Chemistry, compiled for the Use of Students of the Mass. Institute of Technology. Pph. 12mo, pp. 58 and viii. Boston, 1884, 1885, 1886, 1887.
1885. Coal Tar, and the Colors Derived from It. *Proc. Soc. Arts, M. I. T.*, 1884-85, 29-33.
1885. Minor [Chemical] Investigations. *Am. Chem. J.*, 7, 114-120.
1885. (With A. W. Allen.) Ueber die Einwirkung der verdünnten Salpetersäure auf die Anilide. *Ber. d. chem. Ges.*, 18, 1995-1999.
1886. (With C. W. Andrews.) The Action of Heat on Liquid Paraffines. *Am. Chem. J.*, 8, 1-9.
1886. (With A. A. Noyes.) On the Action of Heat upon Ethylene. *Id.*, 8, 362.
1887. (With H. J. Williams.) On the Action of Bromine on Isobutylene. *Id.*, 9, 87.
1887. (With C. B. Kendall.) Preparation of Alizarine Assistant and Its Action in Turkey-Red Dyeing. *Textile Record*, 1887, 227.
1887. (With W. D. Livermore.) Ueber die Einwirkung von verdünnter Salpetersäure auf Substituirte Amidverbindungen. *Ber. d. chem. Ges.*, 20, 2268.
1887. (With H. A. Richardson.) Ueber Leinölsäure. *Id.*, 20, 2735.
- 1887-1888. The Dyeing of Cotton Yarn. *Textile Record*. A series of Articles from June, 1887, to March, 1888.
1888. (With H. A. Richardson.) On the Fatty Acids of the Drying Oils. *Am. Chem. J.*, 10, 57.
1888. Character and Effect of Illuminants Present in Coal Gas. *Technology Quarterly*, 11, 30.
1888. Natural Gas. *Proc. Soc. Arts, M. I. T.*, 1887-1888, 74.
1888. Bleaching. A series of articles in the *Textile Record*, beginning May, 1888.
1888. (With A. A. Noyes.) Note on the Butines. *Am. Chem. J.*, 10, 430.
1889. The Composition of Boston Gas. *Am. Gas Light J.*, 50, 303.
1889. Cutch and Its Uses in Textile Coloring. *Textile Record*, 1889, 34, 66.
1890. (With Herbert C. Tuttle.) Lactic Acids and Lactates in Textile Coloring. *Technology Quarterly*, 3, 287.
1890. Carbonization of Wool. *Textile Record*, 11, 64, 96.
1891. Notes upon the Estimation of Chlorine in Electrolyzed Solutions. *Technology Quarterly*, 4, 361.

Dr. Norton's influence on high scholarship at the Institute of Technology was felt in all departments of chemistry. The book of experiments in general chemistry, which he compiled in connection with the late Professor Nichols, has been a most valued aid to instruction at the Institute and has been largely used at other schools.

In organic chemistry his instruction was on a high plane, yet he never lost sight of the importance, in a school of this character, of insisting on the industrial applications of scientific research.

But it was in the teaching of industrial processes where he especially excelled. His lectures were listened to with eagerness by his pupils, who recognized the master who could deal with equal facility with the scientific basis of a process and with its economic merits. His range of subjects in industrial chemistry was very wide. Not only were the textile industries, bleaching, dyeing, printing, pigments, etc., thoroughly taught, but the great industries of the world in their manifold variety received from him exhaustive treatment. His intimate acquaintance with the manufactures and manufacturers in New England kept him in close touch with the progress of all its industries.

Dr. Norton's career as a chemist and teacher is remarkable for the amount and variety of good work which he accomplished in his short span of life, which had not reached two score years at his death. The Institute of Technology, with which his life was so largely identified, lost in his death not only one of its most valued teachers, but one of the most useful members of its faculty. His judgment, both in matters of general policy of the Institute and of the minute details of organization, was always highly prized by his associates.

His personal character was singularly simple, direct and truthful, and was unselfishly devoted to his family, his friends, and his students.

In 1883 Dr. Norton married Alice Peloubet, who, with five children, survives him.

T. M. DROWN.

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## THE CONSTITUTION OF THE LITHIA MICAS.

BY F. W. CLARKE.

Received July 10, 1893.

IN a series of papers published during the past eight or nine years,<sup>1</sup> I have sought to develop the theory that the complex natural silicates are chemically to be considered as substitution derivatives of simple normal salts. For the micas, in particular, a theory has been worked out in detail, partly on general principles, and partly on the basis of experimental evidence, in which the starting point of the series is the normal aluminum orthosilicate  $Al_2(SiO_4)_2$ , with occasional replacements of the orthosilicic groups by the feldspathic group  $Si_3O_8$ . Thus we have the following systematic scheme:

Normal salt.....	$Al_2(SiO_4)_2$
Muscovite.....	$Al_2(SiO_4)_2R'_1$
Biotite.....	$Al_2(SiO_4)_2R''_1R'_1$
Phlogopite.....	$Al(SiO_4)_2R''_1R'_1$
Clintonite.....	$  \begin{array}{c}  O \\  \diagup \quad \diagdown \\  Al-O \quad R'' \\  \diagdown \quad \diagup \\  SiO_4 \equiv R'_1  \end{array}  $

This scheme is modified, however, not only by the assumption that  $SiO_4$  may be replaced by  $Si_3O_8$ , as in the feldspars, but also by other considerations due to the presence of fluorine in many micas, etc., etc. In the cases of the lithia micas, lepidolite, zinnwaldite, cryophyllite, polylithionite, etc., such modification is absolutely necessary; and hitherto it has been covered by the supposition that the fluorine is represented by the univalent group  $AlF_2$ , among the components of  $R'$ .

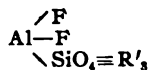
Naturally, and almost necessarily, the development of any such theory is by process of evolution, in which details held provisionally at first are replaced by simpler conceptions, rendered possible by the acquisition of new evidence. A simplification of this order is the purpose of the present communication.

Structurally considered, the lithia micas are all characterized by two special features, an oxygen ratio lower than that of the orthosilicate, and the presence of fluorine. The first of these

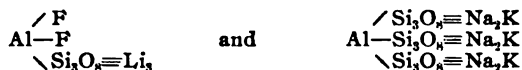
<sup>1</sup> Bulletins of the U. S. Geological Survey, Nos. 27, 42, 55, 60, 64, 78, and 90.



peculiarities has already been explained by the presence of the group  $\text{Si}_3\text{O}_8$ , replacing  $\text{SiO}_4$ , and the second is now rendered intelligible by assuming that the clintonite type may also be replaced by a molecule of the structure



or its equivalent in the corresponding polysilicate. For example, in the polyolithionite described by Lorenzen,  $\text{SiO}_4$  is entirely replaced by  $\text{Si}_3\text{O}_8$ , and the assumption of the latter group is thus fully vindicated. The analogy of the feldspars was strong evidence in its favor; but now we have what may fairly be regarded as positive proof. Polyolithionite may now be considered as a mixture of the two molecules



in the ratio 5:1; whence we get the following comparison between observation and theory:

	Found.	Calculated.
$\text{SiO}_2$	59.25	59.80
$\text{Al}_2\text{O}_3$	12.57	12.70
$\text{FeO}$	0.93	....
$\text{K}_2\text{O}$	5.37	5.85
$\text{Na}_2\text{O}$	7.63	7.72
$\text{Li}_2\text{O}$	9.04	9.34
F	7.32	7.93
	<hr/> 102.11	<hr/> 103.34
$\text{O}=\text{F}$	3.08	3.34
	<hr/> 99.03	<hr/> 100.00

The small amount of ferrous impurity, and the low summation of the analysis, fully account for all the variations between the two columns of figures, both as regards their magnitude and their direction.

In the light of the foregoing evidence, and of the mica theory in general, the lepidolites proper, such as occur in Moravia and in Maine, become easily explainable. All of their variations in composition are covered by the supposition that these micas consist of mixtures in different proportions, of two typical molecules; one the compound  $\text{AlF}_3 \cdot \text{Si}_3\text{O}_8 \cdot \text{R}'$ , with lithium as the principal constituent of  $\text{R}'$ , and the other a muscovitic molecule,

$\text{Al}_2(\text{SiO}_3)_2\text{R}'$ , in which  $\text{R}'$ , may be either  $\text{K}_2\text{H}$  or  $\text{KH}_2$ . Two such mixtures may be considered here: first, the two molecules  $\text{AlF}_3\cdot\text{Si}_2\text{O}_5\cdot\text{Li}$ , and  $\text{Al}_2(\text{SiO}_3)_2\text{K}_2\text{H}$ , in the ratio 1:1; and second, the three compounds  $\text{AlF}_3\cdot\text{Si}_2\text{O}_5\cdot\text{K}$ ,  $\text{AlF}_3\cdot\text{Si}_2\text{O}_5\cdot\text{Li}$ , and  $\text{Al}_2(\text{SiO}_3)_2\text{KH}_2$ , commingled in the ratio 1:2:2. These mixtures correspond to the following percentage compositions:

	First.	Second.
$\text{SiO}_2$	49.05	50.39
$\text{Al}_2\text{O}_3$	27.79	25.70
$\text{K}_2\text{O}$	12.81	13.16
$\text{Li}_2\text{O}$	6.13	5.04
$\text{H}_2\text{O}$	1.22	2.01
F	5.18	6.38
	<hr/>	<hr/>
	102.18	102.68
Less O	2.18	2.68
	<hr/>	<hr/>
	100.00	100.00

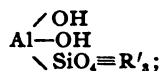
For purposes of comparison with these figures, the following analyses of typical lepidolites are quite sufficient, as they cover all important variations: A, Rozena, by Berwerth; B, Schüttenhofen, by Scharizer; C, Paris, Maine; D, Hebron, Maine; E, Norway, Maine; F, Rumford, Maine. The last four analyses are by Riggs.

	A. <sup>1</sup>	B. <sup>2</sup>	C.	D.	E.	F.
$\text{SiO}_2$ .....	50.98	49.25	50.92	48.80	49.52	51.52
$\text{Al}_2\text{O}_3$ .....	27.80	25.27	24.99	28.30	28.80	25.96
$\text{Fe}_2\text{O}_3$ .....	....	....	0.30	0.29	0.40	0.31
$\text{FeO}$ .....	0.05	0.84	0.23	0.09	0.24	....
$\text{MnO}$ .....	....	0.85	trace	0.08	0.07	0.20
$\text{CaO}$ .....	....	....	trace	0.10	0.13	0.16
$\text{MgO}$ .....	....	....	trace	0.07	0.02	0.02
$\text{Li}_2\text{O}$ .....	5.88	5.38	4.20	4.49	3.87	4.90
$\text{Na}_2\text{O}$ .....	....	0.35	2.11	0.74	0.13	1.06
$\text{K}_2\text{O}$ .....	10.78	13.85	11.38	12.21	8.82	11.01
$\text{Rb}_2\text{O}$ .....	....		trace		3.73	....
$\text{Cs}_2\text{O}$ .....	....		trace		0.08	....
$\text{H}_2\text{O}$ .....	0.96	1.76	1.96	1.73	1.72	0.95
F.....	7.88	5.68	6.29	4.96	5.18	5.80
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	104.33	103.23	102.38	101.86	102.71	101.89
Less O.....	3.32	2.39	2.64	2.02	2.18	2.44
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	101.01	100.84	99.74	99.84	99.53	99.45

<sup>1</sup> Also contains 0.05  $\text{P}_2\text{O}_5$ .

<sup>2</sup> Also contains 0.06  $\text{SnO}_2$ .

In the first of these lepidolites, the mineral from Rozena, a slight variation from the scheme must be assumed, due to the excess of fluorine and the low proportion of alkalis. These peculiarities are easily accounted for by supposing a small admixture of the molecule  $\text{AlF}_3 \cdot \text{Si}_2\text{O}_5 \cdot \text{Al}$ ; which corresponds to the type already indicated, and which is justified by other evidence. In the mineral cookeite, recently re-analyzed by Penfield,<sup>1</sup> we find what appears to be the vermiculite of the lepidolite series; with nearly all the alkalis but lithia removed, and with fluorine replaced by hydroxyl. Penfield's analysis of it reduces easily to the type



and in detail to a mixture of the three molecules  $\text{Al}(\text{OH})_2 \cdot \text{SiO}_4 \cdot \text{Li}$ ,  $\text{Al}(\text{OH})_2 \cdot \text{SiO}_4 \cdot \text{H}$ , and  $\text{Al}(\text{OH})_2 \cdot \text{SiO}_4 \cdot \text{Al}$ , in the ratio 10:14:33. Reducing Penfield's analysis by uniting Fe with Al, the remaining bases with Li, and F with OH, and throwing out water lost at or below 300°, we get the subjoined comparison between observation and theory.

	Found.	Reduced.	Calculated.
$\text{SiO}_2$ .....	34.00	35.01	34.68
$\text{Al}_2\text{O}_3$ .....	45.06	46.71	46.53
$\text{Fe}_2\text{O}_3$ .....	0.45		
$\text{CaO}$ .....	0.04		
$\text{K}_2\text{O}$ .....	0.14	4.29	4.56
$\text{Na}_2\text{O}$ .....	0.19		
$\text{Li}_2\text{O}$ .....	4.02		
$\text{H}_2\text{O}$ below 300°.....	1.82	....	....
$\text{H}_2\text{O}$ above 300°.....	13.14	13.99	14.23
F.....	0.46		
	99.32	100.00	100.00

In the lepidolite from Juschakova, analyzed by Rammelsberg, we find a connecting link between the lepidolites proper and the iron-lithia micas zinnwaldite and cryophyllite. The Juschakova mineral is easily represented as a mixture of molecules like the other lepidolites, except that a portion of the typical  $\text{AlF}_3 \cdot \text{Si}_2\text{O}_5 \cdot \text{R}'$ , is replaced by a similar molecule  $\text{AlF}_3 \cdot \text{Si}_2\text{O}_5 \cdot \text{MnLi}$ . In detail it

<sup>1</sup> *Am. J. Sci.*, May, 1893.

seems to contain the molecules  $\text{Al}_2(\text{SiO}_4)_2\text{K}_2\text{H}$ ;  $\text{AlF}_3\cdot\text{SiO}_4\cdot\text{Al}$ ;  $\text{AlF}_3\cdot\text{Si}_2\text{O}_7\cdot\text{MnLi}$ , and  $\text{AlF}_3\cdot\text{Si}_2\text{O}_7\cdot\text{Li}_2\text{K}$ , in the ratio 2:1:3:6. Calculating its composition upon this basis, we get the following comparison with Rammelsberg's analysis:

	Found.	Reduced.	Calculated.
$\text{SiO}_2$ .....	50.26	50.26	50.33
$\text{Al}_2\text{O}_3$ .....	21.47	21.47	21.39
$\text{MnO}$ .....	5.36	5.36	5.26
$\text{K}_2\text{O}$ .....	11.08	11.08	11.60
$\text{Na}_2\text{O}$ .....	0.54	5.14	5.55
$\text{Li}_2\text{O}$ .....	4.88		
$\text{H}_2\text{O}$ .....	0.66		
$\text{F}$ .....	8.71	9.33	9.38
$\text{Cl}$ .....	1.16		
	104.12	103.30	103.95
Less O.....	3.92	3.92	3.95
	100.20	99.38	100.00

As for the iron-lithia micas, zinnwaldite and cryophyllite, a detailed discussion now would be premature; for the reason that alternative formulae, agreeing equally well with the recorded analyses, are possible. The complication is due to the iron, which may be regarded either as belonging to a molecule of the type  $\text{AlF}_3\cdot\text{Si}_2\text{O}_7\cdot\text{Fe}''\text{R}'$ ; or to a biotitic molecule  $\text{Al}_2(\text{SiO}_4)_2\text{Fe}''\text{R}'$ . The zinnwaldite analyses of Berwerth and Rammelsberg are easiest interpreted as representing mixtures of  $\text{AlF}_3\cdot\text{Si}_2\text{O}_7\cdot\text{FeLi}$ , and  $\text{Al}_2(\text{SiO}_4)_2\text{K}_2$ , in the ratio 5:2, approximately. Cryophyllite, on the other hand, according to analyses by Riggs, is most simply represented by the composition

$\text{Al}_2\text{X}_2\text{KH}_2 + 2(\text{Al}_2\text{X}_2\text{Fe}_2\text{H}_2) + 3(\text{AlF}_3\cdot\text{X}_2\text{K}_2) + 4(\text{AlF}_3\cdot\text{XLi})$ ; in which X corresponds to the two acid groups  $\text{SiO}_4$  and  $\text{Si}_2\text{O}_7$ , in the ratio 1:3. This interpretation is based in part upon the fact that cryophyllite occurs in margins upon plates of annite, which is a lepidomelane of the biotite type. The iron in cryophyllite, however, may also be regarded as present in the molecule  $\text{AlF}_3\cdot\text{Si}_2\text{O}_7\cdot\text{Fe}''\text{R}'$ , as in zinnwaldite; and between this interpretation and the other there are no adequate grounds for deciding. Taking the formulae as given above, Rammelsberg's

analysis of zinnwaldite, and the mean of Riggs' three analyses of cryophyllite compare as follows:

	Zinnwaldite.		Cryophyllite.	
	Found.	Calculated.	Found.	Calculated.
SiO <sub>2</sub> .....	46.44	47.55	51.86	51.95
Al <sub>2</sub> O <sub>3</sub> .....	21.84	21.19	16.50	18.13
Fe <sub>2</sub> O <sub>3</sub> .....	1.27	....	2.98	....
FeO.....	10.19	13.60	6.65	7.52
MnO.....	1.57	....	0.21	....
CaO.....	....	....	0.04	....
MgO.....	0.18	....	0.07	....
Li <sub>2</sub> O.....	3.36	2.84	4.89	4.71
Na <sub>2</sub> O.....	0.54	....	0.79	....
K <sub>2</sub> O.....	10.58	10.66	10.61	12.26
H <sub>2</sub> O.....	1.04	....	1.29	1.41
F.....	7.62	7.18	7.08	6.94
	104.63	103.02	102.97	102.92

In general, it seems highly probable that the lithia micas are all characterized by the presence of the groups  $\text{AlF}_3 \cdot \text{X} \cdot \text{R}'$ ,  $\text{AlF}_3 \cdot \text{X} \cdot \text{R}''\text{R}'$ , and  $\text{AlF}_3 \cdot \text{X} \cdot \text{Al}$ ; in which X may be either  $\text{SiO}_2$  or  $\text{Si}_2\text{O}_5$ , and with the fluorine replaceable by hydroxyl in the process of vermiculitization. In the original form of the mica theory, the group  $\text{AlF}_3$  was regarded as the equivalent of  $\text{R}'$  in a molecule of the muscovite type. It is now represented as belonging to a distinct molecule analogous to clintonite. So far as the evidence goes, this interpretation seems to be satisfactory; and it is an advance upon the earlier scheme in the direction of simplicity.

## CHEMICAL NOTES FROM THE COLUMBIAN EXPOSITION.

### I.

By J. H. LONG.

Received August 2, 1893.

THE various exhibits of the Exposition in Chicago are grouped under twelve heads or departments. Those specially interesting from a chemical standpoint are found in the departments of Agriculture (A), Mines, Mining and Metallurgy (E), Manufactures (H), Electricity and Electrical Appliances (J), and Liberal Arts and Education (L). Certain departments occupy special buildings. The exhibits in several departments are scattered through a number of buildings.

In order to convey a clear idea of what chemistry has done to make the Exposition interesting and instructive it will be found best to study the departments separately, and in the order given above. In most instances it is not my intention to go into details but to sketch in outline what is shown.

DEPARTMENT A.—AGRICULTURE.

We have here really three classes of exhibits, with interest for chemists. The first illustrates chemical methods applied to agriculture, the second the materials which chemistry has given to the farmer to increase production, and the third the results obtained both in the experimental station and on the farm. The application of chemical science to the solution of agricultural problems is of comparatively recent origin and several of the transatlantic countries had taken long strides in this direction before a beginning even was made in the United States. The work of Lawes and Gilbert, Boussingault, Koenig, Maerker and others, following the pioneer investigations of Liebig in time produced its effect this side of the ocean and the Fair at Jackson Park shows what has been done since enthusiasm in the United States was first aroused.

As long as great tracts of virgin prairie or timber soil lay at the disposition of the farmer for little more than the mere asking, and as long as crops of some sort could be raised on this soil with comparatively little labor it was useless to ask the husbandman to follow a rational system in his field or dairy. A few crops could be easily raised and these brought a fair price and there was but little outside competition; why, therefore, try anything new? But times change; fast steamers and cables under the sea have brought the people of the earth near together. The American farmer found new markets for his produce, but he found, also, new competition to meet and the men of science were called in to help him. Agricultural colleges and experimental farms have sprung up all over the country and the work in them has been stimulated by grants from the national government and by strong suggestive influences growing out of the association of agricultural chemists from all parts of the union. Forty-nine of these experiment stations are regularly endowed with an annual grant of \$15,000 each from the general govern-

ment, besides a greater or less sum from other sources, while other stations from time to time receive special endowments for special work.

The chemical division of the Department of Agriculture at Washington has done most excellent work and its exhibit attracts no little attention. This division has published thirty-seven bulletins, of which number 13 appears in parts, eight of which are out with probably four to follow. Several of these bulletins have become standard authorities on special topics. The Department has erected a model laboratory in the north-east corner of the government building and in it are shown apparatus and processes for numerous exact determinations. Some of the equipment is new and some was brought from the Washington laboratory. The interested visitor will find here among other things a large model Landolt polariscope (by Schmidt and Haensch) and an attachment for this or similar instrument for production of constant homogeneous light (see March number of this Journal).

Also apparatus for sampling and analysis of mother beets; apparatus for evaporation of liquids at low temperatures; apparatus for recovery of alcohol; apparatus for cutting green fodders for analysis; a laboratory work table of special design with drainage toward the center; steam vacuum and pressure pumps and several small pieces of apparatus recently designed.

As is well known the laboratory has given much attention to the sugar question, thanks to the lively interest shown by the chief chemist of the Department, Dr. H. W. Wiley, and the exhibit is especially full in appliances employed in the researches in this industry.

In the Agricultural Building the laboratories of the experiment stations have united in making a collective exhibit of considerable interest, but popular, rather than scientific in many features. A model laboratory of an experiment station is shown with practically all the apparatus needed for regular work. There is a good collection of apparatus employed in the analysis of milk and in the examination of water by quick processes. Maps and photographs show the location and character of the important agricultural chemical laboratories of the country, while literature

for free distribution gives information about the work of the leading stations. Once a year the Association of Official Agricultural Chemists holds a meeting, usually well attended by representatives from the laboratories in all parts of the country, at which old and new methods are discussed and at which the "official" processes for various determinations are decided on. The labors of this association have been productive of the highest good and the annual volume of proceedings finds many readers outside of the society. Much of the regular work of the members of the station staffs is published in the *Experiment Station Record*, which is issued at Washington under the auspices of the U. S. Dept. of Agriculture, with Mr. A. W. Harris as Director of Stations. The *Record* is now in its fifth year; it contains original chemical work from home stations, reviews of work done abroad in laboratories and practical results from harvesting of crops.

In the French section of the agricultural building there is a display illustrative of work done in some of the schools and stations of France. There are pieces of apparatus, models, charts, diagrams, maps, and photographs, a large number of books and reports for examination and some literature for distribution.

Dr. Ernest Milliau of the Marseilles Technical Laboratory makes an exhibit of charts in illustration of his methods of testing oils and fats. (See paper in March number of this Journal).

The agricultural schools and stations of Germany and England do not appear to be represented by any independent exhibits. According to the official German catalogue, which should be taken as a model for similar publications because of its concise accuracy and the variety of its information, there are in Germany at the present time fourteen institutions of the highest class in which education in the science of agriculture is given. These comprise the universities and several special institutes. There are thirty-three intermediate schools and 150 in which instruction of an elementary character is given, mainly to sons of peasant farmers, through the winter.

Agricultural chemists will be interested in the display of mineral fertilizers found in the Mining and Agricultural buildings.



In the former are good exhibits of phosphate rocks from Florida and South Carolina, while in the latter are several exhibits of natural and manufactured fertilizers from various sources. The most striking of these is the exhibit of the German Kali works or Stassfurt industry. The main feature of this is a collection of native and recrystallized products from the Stassfurt region, some of them being specimens of rare beauty. The product of the Stassfurt mines is now controlled by a syndicate of nine firms and has grown rapidly in value from a small beginning in 1857. Salt has been produced in the Stassfurt region for the last two hundred years by the evaporation of brine, but this industry had sunk to one of very small importance, when in 1857 borings showed the existence of extensive deposits of potassium and magnesium salts at a depth of 1000 feet or more. These salts were supposed, at first, to have but little value but they have become of the highest importance in chemical industry and in agriculture. The exhibit is arranged in eight groups:

1. Rock-salt of lower stratum, impure.
2. Rock-salt of upper stratum, pure.
3. Carnallite.
4. Kieserite.
5. Sylvin, with NaCl or  $\text{MgSO}_4$ .
6. Kainite.
7. Schoenite.
8. Boracite.

These groups are divided according to the predominating minerals and do not simply contain pure crystals of each species. With rock-salt of the first group anhydrite, polyhalite, sulphur and glauberite are found and are here shown. The rock-salt of the second group from the upper stratum, although nearly chemically pure, is frequently beautifully colored, crystalline and clear. The carnallite of the third group is found pure and mixed with bischofite, kieserite and other minerals. The kieserite of the fourth group occurs pure and mixed with several other compounds. The sylvin of the fifth group and the kainite of the sixth group are exceedingly interesting exhibits as they contain a number of beautifully colored varieties, some of which are rare. In the seventh group two specimens of schoenite and the allied species, leonite, are shown. With the boracite of the

eighth group a number of comparatively rare boron minerals are exhibited. Although about twenty-five species in all, with several varieties, are shown it must not be supposed that all have commercial importance. In fact, at the present time only five of the above-named minerals find application on the large scale, and these are kainite, sylvin, boracite, carnallite and rock-salt.

Kainite is mainly used as a fertilizer and for this purpose is prepared for market by simple grinding. The mineral as mined contains on an average about sixty per cent. of pure kainite. Its value in agriculture depends on the amount of potassium sulphate present, although the combined percentage of magnesium sulphate and chloride is higher. It is therefore sold with a guaranteed amount of potash corresponding to twenty-three per cent. of the sulphate. Small amounts of several purified salts are made from kainite as a starting point. The amount of kainite sold increased from 1313 tons (of 1000 kgms.) in 1865 to 545,084 tons in 1892. Sylvinit, which contains on an average twenty-five per cent. of potassium chloride, sixty-five per cent. of sodium chloride, and seven or eight per cent. of the sulphates of potassium and magnesium, is also used mainly in the manufacture of fertilizers. The production of sylvinit increased from 2220 tons in 1888 to 32,669 tons in 1892. Boracite occurs in lumps usually mixed with carnallite. These lumps are sorted out by hand and sold for the production of borax and boric acid. The crude salt with seventy-five per cent. of boracite guaranteed, was mined to the extent of four tons in 1864 which increased to 205 tons in 1883, and 166 tons in 1892. Carnallite is naturally the most important of the Stassfurt minerals and occurs generally mixed with rock-salt and kieserite. The average composition of the crude carnallite, roughly separated from the bulk of salt found with it is :

Carnallite .....	61 per cent.
Rock-salt .....	25 " "
Kieserite .....	12 " "
Anhydrite and clay ....	2 " "

Pure carnallite should have the following percentage composition :

MgCl <sub>2</sub> .....	34.5 per cent.
KCl .....	26.8 " "
H <sub>2</sub> O .....	38.7 " "

from which it appears that the amount of  $KCl$ , the most valuable of the constituents, in the average mineral is 16.5 per cent. It is sold on a guarantee of 14.3 per cent., usually, and is employed in the crude form to some extent as a fertilizer, but most of it is used in certain industries whose reputation is world wide and which will be referred to later. In 1882, 5590 tons of carnallite were used as a fertilizer directly, while 1,053,709 tons were converted into purified salts. In 1892, 40,114 tons of crude carnallite were used in Germany as a fertilizer, and 723 tons were exported for the same purpose, while 695,912 tons were converted into concentrated salts. Immense quantities of potassium chloride are made, the amount being about 125,000 tons annually during the last fifteen years; a part of this is employed in agriculture, and the rest in chemical industry, mainly in making saltpeter by double decomposition with sodium nitrate. Several crude mixtures containing potassium salts are made from carnallite and are sold as fertilizers. They contain from fifteen to forty per cent. of potash ( $K_2O$ ). The mining of rock-salt at Stassfurt is still a very important industry notwithstanding the constantly increasing amounts of salt produced elsewhere. The amount mined in 1857 was 12,797 tons, with a pretty regular increase down to the present time. In 1890 the product was 302,205 tons, in 1891, 365,910 tons, and in 1892, 293,247 tons. Some of this is very pure, 99 to 100 per cent., and serves for the production of fine white table salt, butter and pickle salt. The coarser and less pure grades are sold for salting cattle and for various chemical purposes.

The Mining building contains a small exhibit of Stassfurt minerals, but other nations make only very small exhibits of fertilizers, with the exception of Chile, which shows sodium nitrate in large quantities in crude and manufactured form.

As illustrating the results obtained by the application of chemistry to agriculture we have first in importance among the exhibits those made by the United States experiment stations. They consist of charts, diagrams, and jars filled with animal and vegetable products obtained under certain definite conditions of

fertilization or feeding. Reference must be made also to the full literature of the subject found in the form of bulletins not only in the *Experiment Station Record* but sent out as independent publications by the states themselves. The work of the Rothamstead laboratory and farm is illustrated by several charts displayed with the United States station exhibits. These were sent by Messrs. Lawes and Gilbert. It appears that the most valuable part of the exhibit sent by them has been lost on the way.

In the French section there are numerous charts illustrative of results gathered from the experimental farms of France. Brief mention must be made of several industrial exhibits which have a certain interest from the chemical standpoint. Starch and starch sugar are displayed by five American firms; one French firm sends rice starch, but Germany, England, Austria, and other European countries are not represented here. The chemical features of the cane-sugar industry are poorly illustrated in the United States displays. Nebraska makes an interesting exhibit of beet sugar. Two factories are in operation in that state, and the amount of refined sugar they put on the market in 1892 was nearly 4,000,000 pounds. Indications are that a much greater yield will be marketed this season. Photographs of the sugar machinery at the works are shown. It has been demonstrated that the soil and climate of Nebraska and other states are well adapted to the culture of the beet; the chemical division of the Department of Agriculture is able and ready to render all needed scientific aid, but the question of labor is the perplexing one which must be solved before the United States can think of supplying its own demand for sugar. No sugar is found in the exhibits of Austria or Germany, but some of the British colonies, Belgium, France, Italy, Russia, and the countries of Central and South America, make good displays. Interesting photographs of the machinery and other parts of one of the large Russian factories are shown and are quite worth examination. Edible oils and certain other refined products are found in abundance in the agricultural display, but their description is beyond the scope of this article. The samples of olive oil sent by California indicate that the industry is a growing one in that state.

## MINES, MINING, AND METALLURGY.

The exhibits in this department are divided into twenty-seven groups, 42 to 68 inclusive, and there is scarcely one, which in some degree at least, is not interesting to chemists. In this general survey of the field I shall attempt to touch upon only those which are important as in some measure involving chemical processes.

First among these in the catalogue order is the elaborate display of the Standard Oil Company, of Cleveland. Everything connected with the industry of collecting and refining oil is represented here by profile maps, models of plants, samples of various crude oils, samples of light and heavy refined oils and other products. The list of refined products is large and instructive. Various mineral oils, crude and refined, are found in the displays of several states, notably from New York, Pennsylvania, Ohio, and Indiana. Crude mineral oils and asphalts are found in the displays of California, Utah, and Wyoming. Chemists interested in the asphalt industry will find good exhibits from the French, Swiss, Trinidad, and western American districts. Portland and other cements and the materials from which they are made are shown by American, German, French, and English exhibitors. In the German section of the Mines building there is a well-equipped cement testing laboratory, with all necessary appliances for chemical and physical examinations.

It would be useless to attempt a description of metals and ores, which are the chief attraction in this department, but special attention must be called to a few which are of unusual interest. Johnson, Matthey and Company, London, exhibit metals of the platinum group in crude and manufactured form. There are several large pieces of platinum and gold-lined platinum apparatus for the concentration of sulphuric acid, various smaller vessels for laboratory use, a standard meter of platinum-iridium and a number of rods and bars employed in tests of coefficients of expansion, etc. There are shown, also, an ingot of palladium weighing 1,000 ounces and valued at £7,000, an ingot of iridium weighing 240 ounces, large samples of rhodium, osmium, ruthenium and a number of rare salts of some of these metals. The Deutsche Gold und Silber-Scheide-anstalt of Frankfurt am Main,

makes a very good display of gold, silver, and lead products, also colors for pottery, assaying chemicals and apparatus. Attention must be called in this place to the exhibit of W. C. Heraeus of Hanau, found in the manufactures building; more will be said about it in the proper place. The Canadian Copper Company, of Ontario, shows in large quantities nickel ores, alloys and pure metal. Like many other important exhibits this one appears to have been overlooked by the catalogue maker. The exhibit of the Pittsburgh Reduction Company, of aluminum and alloys and process of reduction is a creditable one and worthy of study. A model of the electric furnace used in the plant at Kensington, near Pittsburg, is shown. Assayers will find a well-equipped laboratory in this building furnished with modern appliances as used in the United States. Several men are at work here and ready to make all explanations asked for. In the exhibits of Utah, Wyoming, New Mexico, and Montana are several minerals which when compared with the great ore displays may appear of little importance, but which, however, are worthy of consideration. It is not popularly known, although described in bulletins of the United States Geological Survey, and recently at length in bulletin 60, that in the localities named there are vast beds of salts, sometimes nearly pure, but frequently mixed, which in time must play an important part in the industries of this country. Sodium sulphate exists, especially in Wyoming, in beds of great extent, sometimes crystalline and sometimes effloresced and nearly dry. The bulletin referred to gives analyses of this substance. I give here two analyses of native samples, which represent, I am told, large deposits. The analyses were made in my laboratory:

	1.	2.
$\text{Na}_2\text{SO}_4$ .....	97.20	97.36
$\text{NaCl}$ .....	0.59	0.14
$\text{Na}_2\text{CO}_3$ .....	0.04	....
$\text{CaSO}_4$ .....	0.58	0.75
$\text{MgSO}_4$ .....	0.85	1.26
$\text{H}_2\text{O}$ and loss .....	0.74	0.49
	<hr/> 100.00	<hr/> 100.00

I have seen samples of even greater purity. Much of the sulphate is mixed with carbonate, over fifty per cent. of the latter

being frequently present in effloresced condition. Attempts have been made to manufacture pure alkali from this, but up to the present time without marked success (see in this connection an article by Professor Lunge, *Ztschr. angew. Chem.*, January, 1893). During the present year a new company has begun operations in Wyoming and has already achieved results which point to success in the future. Magnesium sulphate is also found in quantity in parts of Wyoming, but the absence of good railroad facilities renders all these deposits of little value at the present time. As coal seems to be found in abundance in the vicinity of some of these beds their development is one of the certainties of the future.

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### SOME EXPERIMENTS ON SAMPLING BY QUARTATION.

By P. W. SHIMER AND S. K. REIFSNYDER.

FOR reducing the bulk of a coarsely crushed sample of ore on the laboratory sampling table preparatory to still finer crushing, it is customary to mix, spread out, and quartate the sample once or oftener. In order to determine the degree of accuracy obtainable by this procedure, as well as to discover, if possible, the best way to manage the details of mixing and quartation, the following experiments were made upon a mixture of 500 grams lead shot just large enough to be retained by a ten mesh sieve; 500 grams magnetic iron ore of a size between ten mesh and twenty mesh and 500 grams of crushed glass passed through a twenty mesh sieve, but from which the finest powder had been removed by washing with water. By reason of the different sizes, shapes, and specific gravities of the elements of this mixture it is a very difficult one to sample.

It was conceived, therefore, that any inaccuracy in the results of sampling would be prominently brought out and that any method that would give good results on this mixture, could be confidently used on the less difficult mixtures occurring naturally in ores. The mixture of 500 grams each of shot, magnetite, and glass was first separated by sifting, with the result that it was found to be possible to recover the exact amount ( $33\frac{1}{3}$  per cent.) of each from the mixture. 500 grams of each were again

mixed on a large paper, using forty motions of the paper. The mixture was then spread out with a spatula and quartated, in the usual manner, with the following results :

	No. 1.	No. 2.
Shot.....	33.8 per cent.	33.1 per cent.
Ore.....	34.1 " "	32.3 " "
Glass.....	32.2 " "	34.6 " "

Each of these parts was then mixed, spread out, quartated, sifted, and weighed as before and the process was continued until each constituent of the mixture had been reduced to sixty grams; the results, grouped together, were as follows :

Shot (per cent.).....	38.6	28.7	37.7	39.5	28.4	29.0	34.7	31.8	31.7
Ore " " .....	32.0	36.0	33.7	31.6	37.1	34.5	31.6	32.9	32.9
Glass " " .....	39.4	35.3	28.6	28.8	34.5	36.5	33.7	35.3	35.3
Shot (per cent.).....	37.5 35.3 28.4								
Ore " " .....	29.8 31.4 34.6								
Glass " " .....	32.7 33.3 37.0								

The results seem to vary more widely from the truth the further the sample is reduced by quartation. Having now ascertained how inaccurate the results may be when obtained by the above method, some variations, suggested by the course of the work, were tried. In all the experiments which follow the sampling was not carried beyond the first quartation.

By mixing with forty motions of the paper, spreading out with a spatula, and quartating, the results were :

Shot (per cent.).....	34.3	32.4	32.4
Ore " " .....	32.0	34.6	35.8
Glass " " .....	33.7	33.0	31.8

To compare with these, three quartations were made by moistening with water, mixing forty times, spreading out with spatula, and quartating. The results were :

Shot (per cent.).....	31.8	32.0	31.0
Ore " " .....	33.7	33.2	34.7
Glass " " .....	34.5	34.8	34.3

Averaging these results, we have :

	Sampled dry.	Sampled moist.
Shot.....	33.0	31.6
Ore.....	34.2	33.9
Glass.....	32.8	34.5



The slight advantage in favor of the dry mixing was unexpected and led to the suspicion that the spreading out of the sample by means of the spatula was the cause of the trouble. In the next experiments, instead of using the spatula, the sample, after mixing, was simply flattened out by pressure under a small, smooth board. Assuming that the mixture is perfect at the end of the mixing it seemed probable that spreading out with a spatula might destroy the uniformity of the mixture, while, by simply flattening out the sample by means of the board, the relative positions of the particles would remain practically unchanged.

By mixing forty times dry, flattening, and quartating, the results were :

Shot (per cent.)	....	32.0	35.7	32.9	32.3	32.9
Ore    "    "	....	35.0	31.9	33.5	33.7	33.9
Glass "    "	....	32.9	32.4	33.6	34.0	33.1

By mixing forty times moist, flattening, and quartating, the results were :

Shot (per cent.)	.....	32.9	32.8	31.8
Ore    "    "	.....	33.5	33.5	34.1
Glass "    "	.....	33.6	33.7	34.1

By mixing forty times dry, then forty times moist, flattening, and quartating, the results were :

Shot (per cent.)	.....	33.1	33.5
Ore    "    "	.....	33.5	33.4
Glass "    "	.....	33.4	33.1

The average of the four best dry is: Shot, 32.6; ore, 34.0; glass, 33.4. The average of the four best moist is: Shot, 33.1; ore, 33.5; glass, 33.4. The average of the two mixed forty times dry and forty times moist is: Shot, 33.3; ore, 33.45; glass, 33.25.

From the preceding experiments it appears that there is an advantage in mixing moist, both in accuracy and neatness. Decidedly better results are also obtained when the mixture is simply flattened out with a board instead of being spread out with a spatula. The best results also seem to be obtained when the sample is first mixed dry, then moistened and mixed again, for when dry there is greater freedom of motion among the particles. When, however, the sample is well mixed dry it should

be moistened and mixed again, not only to obtain a still more uniform mixture, but to maintain it during quartation.

Wishing to verify these conclusions in the case of an ore, a sample of crushed iron ore was obtained containing in its coarser portions considerable hornblende and in its finer portions a larger proportion of magnetite. The sample was divided into four sizes by careful sifting.

	Per cent.
Between 4 and 6-mesh sieves.....	34.69
"    6    "    10-mesh    "    .....	18.47
"    10    "    20-mesh    "    .....	14.10
Through 20-mesh sieve .....	32.74

Four hundred grams of each size were taken, mixed dry, and spread out very thin with the spatula before quartation. Instead of twenty-five per cent. of each, we found :

	Per cent.
Over 6-mesh sieve .....	27.0
"    10-mesh    "    .....	25.4
"    20-mesh    "    .....	24.5
Through 20-mesh sieve .....	23.1

Another mixture was made in the same manner, using the spatula, but not spreading out the heap so thin as before.

	Per cent.
Over 6-mesh sieve .....	25.6
"    10-mesh    "    .....	24.8
"    20-mesh    "    .....	24.5
Through 20-mesh sieve .....	25.1

The following were then mixed dry sixty times, flattened by use of the board, and quartated.

	Per cent.	Per cent.	Per cent.
Over 6-mesh sieve.....	23.6	25.4	25.1
"    10-mesh    "    .....	25.7	25.0	25.2
"    20-mesh    "    .....	26.3	24.4	25.0
Through 20-mesh sieve...	24.4	25.2	24.7

Mixing thirty times dry and thirty times moist, flattened, and quartated :

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Over 6-mesh sieve .....	24.5	25.1	24.0	25.7	25.4
"    10-mesh    "    .....	25.4	24.9	24.3	25.3	24.8
"    20-mesh    "    .....	25.4	25.0	26.1	24.4	24.9
Through 20-mesh sieve ....	24.7	25.0	25.6	24.6	24.9

By mixing fifty times dry, then fifty times moist, flattening, and quartating, the results were:

	Per cent.
Over 6-mesh sieve .....	25.8
" 10-mesh " .....	24.9
" 20-mesh " .....	24.6
Through 20-mesh sieve .....	24.7

The average of dry and moist results were:

	Dry, per cent.	Moist, per cent.
Over 6-mesh sieve .....	24.7	24.9
" 10-mesh " .....	25.3	24.9
" 20-mesh " .....	25.2	25.2
Through 20-mesh sieve .....	24.8	25.0

A few determinations were then made by a method sometimes used. The ore was carefully mixed as before and halved by allowing a small scoop full of the ore to fall over a thin partition. The results of these separations were:

	Dry			Moist.
	Per cent.	Per cent.	Per cent.	Per cent.
Over 6-mesh sieve .....	25.7	26.0	25.5	24.3
" 10-mesh " .....	26.6	25.6	26.0	24.7
" 20-mesh " .....	24.0	24.8	24.9	25.7
Through 20-mesh sieve .....	23.7	23.6	23.6	25.3

These results are not so good as those obtained by quartation, but here, as before, the moist method has the advantage in accuracy and neatness.

The four sizes were then separately prepared for analysis, the results showing the percentages of metallic iron soluble in hydrochloric acid (magnetite) and insoluble in hydrochloric acid (hornblende) are as follows:

	Per cent. Over 6-mesh.	Per cent. Between 6 and 10-mesh.	Per cent. Between 10 and 20-mesh.	Per cent. Through 20-mesh.
Soluble in HCl.....	30.30	28.57	27.31	40.25
Insoluble in HCl .....	8.65	8.85	9.18	6.25
Total metallic iron.	38.95	37.42	36.49	46.50

The amount of iron in the different sizes is seen to vary considerably. Knowing the percentage of each grade in the original sample and the percentage of iron in each grade, the percentage of iron in the original sample is readily found to be 40.78. A sample of the mixture experimented on, containing

twenty-five per cent. of each size, should contain by calculation 39.835 per cent. metallic iron. Calculating the amount of iron in the first (dry) sample, which is a very poor one, having been spread out thin with a spatula, we find the sample would yield 39.699 per cent. iron, thus causing an error of 0.136 per cent. While this sampling error is notable, it must be remembered that this error would be increased very much if the quartations were carried further, as was shown by the preliminary work. Taking the average results dry we find an error of 0.022 per cent. Taking the average results moist we find an error of 0.006. The error in the percentage of iron ranges from 0.136 per cent. to 0.006 per cent., the greater error coming from a sample made dry and the least from one made moist. In the average results there is a difference of 0.016 per cent. in favor of moist sampling. This fact agrees with the result of an investigation on the moist sampling (with alcohol) of cast-iron borings published by one of the writers some years ago (*Trans. A. I. M. E.*, 14, 760). The results may be briefly recapitulated as follows:

- (1) It is more accurate to sample moist than to sample dry.
- (2) Moist sampling is preferable because of neatness of separation and absence of dust.
- (3) It is better to mix dry, then moisten, and mix thoroughly again before quartating.
- (4) It is far better to flatten out the sample by simple pressure than to spread it out by means of a spatula.

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#### THE ANALYSIS OF LUBRICATING OILS CONTAINING "BLOWN" RAPE-SEED AND "BLOWN" COTTON-SEED OILS.

BY THOS. B. STILLMAN, PH.D.

Received August 8, 1873.

**R**APE-SEED oil has long been the standard oil in Europe for lubrication. Its constancy of viscosity at varying temperatures, its non-liability to acidity as compared with other seed oils, and its low cold test, unite in producing the results required of a good lubricant. It, however, is no exception to the rule that vegetable and animal oils suffer partial decomposition when subjected to high temperature produced by friction,

with a result that fatty acids are liberated and corrosion of bearings produced.

The substitution of mineral oils in varying proportions with rape-seed oil has reduced this tendency, this reduction being determined by the percentages of mineral oil present, as the latter liberates no free acids.

It is a peculiar fact, however, that a mineral oil alone does not give as satisfactory results in lubrication (especially cylinder lubrication<sup>1</sup>) as does a mixture of mineral and vegetable or mineral and animal oils, one of the primary causes being that the viscosity of mineral oils rapidly diminishes at high temperatures, whereas the reduction of viscosity of vegetable and animal oils is very much less.

If it were not for this peculiarity between these two classes of oils, mineral lubricating oils could easily supplant (on the score of cheapness) all other oils used in lubrication.

The admixture of oils then being required for the better class of lubricants, it follows that in England where rape-seed oil has been the standard, its use should be continued in compounded oils.

The proportion of rape-seed oil added to mineral oil varies from five to twenty per cent. Where the mineral oil is a clear paraffin oil twenty per cent. of the seed oil is used; where the mineral oil is a dark, heavy oil, five per cent. is generally added.

The separation and estimation of the rape-seed oil in these mixtures presents no difficulty to the analytical chemist when no other seed oil is present, since the saponification of the seed oil, the separation of the fatty acids and recognition of the same are a part of the usual chemical work of this character. The recognition of the constituents of a mixed lubricating oil by analysis is a very different problem from giving a formula by which the mixture can be made. This is evidenced as follows:

Suppose the analysis shows

Rape-seed oil, 20 per cent.

Paraffin oil, 80 per cent.

Paraffin oil varies in specific gravity from 0.875 to 0.921, and it is essential to include in the report of the analysis not only

<sup>1</sup> *The Railroad and Engineering Journal*, 64, 73-126.

the amount of the paraffin oil but also the gravity, since paraffin oil of gravity 0.875 is a very different product from that of 0.921 gravity, the former selling at seven and one-half cents and the latter at twenty-three cents per gallon. This determination can be made by taking the gravity of the original mixed oil (0.912), then knowing by analysis that twenty per cent. is rape-seed oil (gravity 0.918), the gravity of the eighty per cent. of paraffin oil is easily calculated. Thus:

$$\begin{aligned} x &= \text{specific gravity of rape-seed oil (0.918)} \\ y &= \text{specific gravity of paraffin oil} \\ x &= 20 \text{ per cent. or } \frac{1}{5} \\ y &= 80 \text{ per cent. or } \frac{4}{5} \\ \text{Then } \frac{1}{5}x + \frac{4}{5}y &= 0.912 \\ 0.183 + \frac{4}{5}y &= 0.912 \\ \frac{4}{5}y &= 0.729 \\ y &= 0.910 \\ \text{The mixture being composed, therefore, of} \\ \text{Paraffin oil (sp. gr. 0.910), 80 per cent.} \\ \text{Rape-seed oil (sp. gr. 0.918) 20 per cent.} \end{aligned}$$

The direct determination by analysis from the ether solution of the mineral oil in the mixture does not give an oil of the same specific gravity as the mineral had before it was mixed with the seed oil. This can be accounted for by the volatilization of a portion of the lighter hydrocarbons of the mineral oil when the ether is expelled during the analysis. For this reason the determination of the percentage of seed oil and the calculation of the mineral oil offers less liability to failure than finding the mineral oil directly.

The introduction of "blown" rape-seed oil instead of the normal rape-seed oil complicates the investigation and renders the use of the formula above given valueless. Rape-seed oil has a gravity of 0.915 to 0.920. Rape-seed oil "blown" has a gravity of from 0.930 to 0.960.

Two difficulties are immediately presented: (1) The chemical analysis does not indicate whether the rape-seed oil is "blown" or not; (2) The use of the formula given without the correct gravity of the "blown" oil would give false results regarding the paraffin oil. To overcome this difficulty some synthetical work is required.

Suppose the specific gravity of the mixed oil is 0.922 and the analysis shows twenty per cent. of rape-seed oil. It will be necessary then to produce a mixture in these proportions that will duplicate the original sample. A check upon this will be the viscosity of the original sample as compared with the one to be made by formula: Thus:

The original oil has a gravity of 0.922, contains (by analysis) twenty per cent. of rape-seed oil, and has a viscosity at 100° F. of 335 seconds (Pennsylvania Railroad Pipette).

*First.*—Make a mixture of paraffin oil (sp. gr. 0.910), generally used in this character of lubricant, eighty per cent., and rape-seed oil ("unblown") twenty per cent. The viscosity is 165 seconds, showing that this mixture can not be used in place of the original oil.

*Second.*—Make a mixture of paraffin oil (sp. gr. 0.910) and rape-seed oil (partially blown, sp. gr. 0.930) in the same proportions as above. The resulting viscosity is 267 seconds, showing that the compound is still lacking in viscosity.

*Third.*—Make a mixture of paraffin oil (sp. gr. 0.910) eighty parts, and rape-seed oil, "blown," (sp. gr. 0.960), twenty parts. The viscosity is 332 seconds.

This now fulfills the conditions required and the synthetical sample agrees with the original in gravity, composition and viscosity.

The use of "blown" rape-seed oil is being gradually replaced by "blown" cotton-seed oil. The latter, which has had but a limited use in lubrication, owing to its liability to acidity, has been greatly improved by this process of "blowing," which is nearly complete oxidation of the oil under comparatively high temperature.

This largely prevents the occurrence of the acidity in the oil, and thus the main objection to its use in lubrication disappears. It is much cheaper than rape-seed oil, since it costs forty cents per gallon, to seventy cents per gallon for the latter. The chemical reactions of the two oils are very similar, and careful analytical work is required that the chemist be not misled.

The following table of comparisons will indicate this:

## SPECIFIC GRAVITY.

Cotton-seed oil .....	0.920 to 0.925
Rape-seed oil .....	0.915 to 0.920
"Blown" cotton-seed oil .....	0.930 to 0.960
"Blown" rape-seed oil .....	0.930 to 0.960

## VISCOSITY (PENNSYLVANIA RAILROAD PIPETTE) AT 100° F.

	Seconds.
Cotton-seed oil (sp. gr. 0.925) .....	165
Rape-seed oil (sp. gr. 0.918) .....	210
"Blown" cotton-seed oil (sp. gr. 0.960)....	2143
"Blown" rape-seed oil (sp. gr. 0.960) .....	2160

## HEIDENREICH'S TEST.

	Before stirring.	After stirring.
Cotton-seed oil .....	Faint reddish brown.	Brown.
Rape-seed oil .....	Yellow brown.	Brown.

## MASSIE'S TEST.

Cotton-seed oil .....	Orange red.
Rape-seed oil .....	Orange.

## IODINE ABSORPTION.

Cotton-seed oil .....	104 to 114
"Blown" cotton-seed oil .....	93 to 103
Rape-seed oil .....	102 to 108
"Blown" rape-seed oil .....	94 to 100

In the comparison of the two oils, when not mixed with a mineral oil, the above tests can be used. The conditions are altered, however, when either one or both are so mixed, since these tests apply only to the pure oils and not to those reduced with large percentages of mineral oil. After the separation of the seed oil from the mineral oil by saponification the identification of the seed oil depends upon the reactions of the fatty acids obtained, and a careful examination and comparison of these reactions shows that the melting points have the greatest difference and thus become a means of recognition.

Thus, the fatty acids from rape-seed oil melt at 20° C., and from cotton-seed oil at 30° C. Hence, if upon analysis of a lubricating oil under above conditions, the fatty acids obtained show a melting point of 20° C. the seed oil can be pronounced rape-seed oil.

If the melting point is between these limits, say 23° C., the seed oils are present in a mixture, the proportions of which can be determined by the following formula:



$w_1$  = proportion of rape-seed oil

$w_2$  = proportion of cotton-seed oil

$w_3$  = weight of mixture (20 per cent.)

$t_1$  = temperature of melting point fatty acids of rape-seed oil.

$t_2$  = temperature of melting point fatty acids of cotton-seed oil.

$t_3$  = temperature of melting point of mixed fatty acids.

$$\text{Then } w_1 = w_3 \frac{t_3 - t_2}{t_1 - t_2}$$

$$w_2 = w_3 \frac{t_3 - t_1}{t_2 - t_1}$$

Inserting the values :

$$w_1 = 20 \frac{23-30}{20-30} = 14 \text{ per cent.}$$

$$w_2 = 20 \frac{23-20}{30-20} = 6 \text{ per cent.}$$

Or,

Paraffin oil ..... 80 per cent.

Rape-seed oil ..... 14 per cent.

Cotton-seed oil ..... 6 per cent.

Total ..... 100 per cent.

By synthetical work upon these proportions, with comparison of viscosities of the sample submitted with the product, the result will be not only a correct analysis, but a working formula can be given by which a manufacturer can duplicate the original oil.

STEVENS INSTITUTE OF TECHNOLOGY,  
AUGUST 8, 1893.

## AN AUTOMATIC EXTRACTOR.

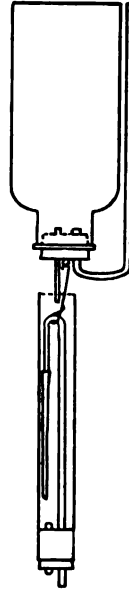
By W. D. HORNE.

Received August 7, 1893.

IN the analysis of commercial fertilizers soluble phosphoric acid is separated by repeated washings of the mass with small quantities of water. Two grams of the sample are treated on a ribbed filter with successive portions of water, about ten cc. at a time, until at least 250 cc. have run through, each addition being deferred until the preceding has passed through.

Feeling that time might be saved by having this washing done automatically led to the device of a simple apparatus which mechanically delivers the required quantity of water at measured intervals in a gentle stream upon the material on the filter, stirring it up and leaching out the soluble matter without requiring any attention after the start.

One part of the apparatus consists of a wide-mouthed bottle of 250 cc. capacity closed by a cork perforated by two glass tubes. One tube projects outward about three or four cm. and tapers to a moderately fine point. The other tube, after emerging from the cork, curves directly over the edge of the cork and extends down the full length of the bottle on the outside. The bottle, being filled with water, is inverted, and the water drops from the end of the short tube, while the necessary air enters by the long bent tube and bubbles up through the column of water in the bottle. As the rate of flow or dropping depends principally upon the fineness of the point of the dropping tube and the freedom of the air's access through the longer tube, any desired rapidity of flow can be obtained by varying the size of either tube. It is more advantageous to use the same dropper and to regulate the air supply by plugging more or less loosely the upper end of the air tube with an appropriate stopper.



So much for the water supply. In order to convert this into an intermittent washing stream it flows into a tube suspended below, provided with a capillary siphon tube within, whose longer limb passes through a stopper at the bottom of the outer tube, something like the Adams fat extractor.

To make this part of the apparatus, cut the bottom off of a test tube fifteen mm. in diameter and fifteen cm. long, close one end with a rubber stopper with one hole, and within the test tube put a three mm. tube bent double by a sharp curve, with one limb about fifteen cm. long and the other about three cm. The longer limb passes through the hole in the stopper at the bottom of the test tube, while on the shorter limb is put a piece of rubber tubing of variable length, according to the quantity of water that is to be siphoned off at each delivery. To the loop of the siphon fasten one end of a short wire, whose other end terminates in a hook to catch in a wire eye inserted in the cork of the inverted bottle.

Thus suspend the siphon apparatus to the water supply, having the dropping tube inside the test tube. When the water is allowed to drop the test tube slowly fills, until the water, rising in the siphon's short arm, passes beyond the bend and siphons over. The operation then repeats itself.

The speed of dropping from the reservoir must be such as to allow each siphoned portion to pass completely through the filter before the next flows on. And the quantity which siphons over each time is to be regulated by varying the length of the rubber tube which extends from the short limb of the siphon. The lower end of this rubber tube is cut off diagonally to ensure complete emptying of the siphon at each delivery.

These things once arranged, they need little attention afterwards.

Only a moment is required to fill the bottle, attach the siphon tube, and hang the inverted bottle in its rack with the filter containing the fertilizer below it in a funnel resting in a flask.

The washing is done regularly, without attention and without loss of time. A few supplementary washings by hand may be well to get the material all into the point of the filter, although experiments have shown that the mechanical washing is thorough and gives results identical with the tedious hand method.

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## THE ACTION OF GASEOUS HYDROCHLORIC ACID AND OXYGEN ON THE PLATINUM METALS.<sup>1</sup>

BY WM. L. DUDLEY.

HENRY (*Trans. Roy. Soc.*, 1800, 188) discovered that hydrochloric acid gas, mixed with one-fourth its volume oxygen, passed over platinum black, was decomposed as water formed:  $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ .

While working up some platinum and iridium residues found that finely divided platinum sponge on being washed with hydrochloric acid gave ample evidence of solution. led me to investigate the subject further.

<sup>1</sup> Read before the American Association for the Advancement of Science, Meeting, August, 1893.

Platinum black was put on a filter and moistened with dilute hydrochloric acid. In a few hours the filter paper was stained yellow, and on washing, the filtrate had a yellow color and contained platinic chloride. Very soon, however, the filtrate became clear, even if the washing was continued with hydrochloric acid, but on standing after again moistening with hydrochloric acid, the platinum was dissolved as before, showing that the oxygen of the air was necessary for the decomposition of the hydrochloric acid, and that the platinum was attacked by the nascent chlorine. The action seemed to be most rapid as the filter paper approached dryness. By repeated moistening with hydrochloric acid and exposure to the air, the platinum black would probably have dissolved completely, but I did not carry the experiment to that point.

Platinum sponge was next tried in a similar way, and the result was found to be essentially the same, but not quite so marked.

Platinum black and platinum sponge were each subjected to the action of a dried mixture of hydrochloric acid gas and atmospheric air. Each was attacked by nascent chlorine. The effect on the sponge was, however, much less than on the black. Oxygen was substituted for the air, and the gases were used without being dried, but in each case the result was practically the same as that noted above. The experiment was tried at various temperatures up to  $100^{\circ}$  without any special change in the result. When the temperature reaches the point at which platinum chloride decomposes, chlorine is set free (Jullion, British patent, No. 11425, 1846).

It is well known that finely divided palladium is soluble in hydrochloric acid mixed with oxygen or air (Fischer, *Schw.*, 51, 192, and *Pogg*, 71, 431).

Iridium, rhodium, ruthenium and osmium in finely divided condition were treated in the same way as the platinum and in each case it was found that the metal had the power to cause the union of the oxygen and the hydrogen of the hydrochloric acid, and to combine with the nascent chlorine. The action on ruthenium and osmium was greatly increased on heating, especially at about  $250^{\circ}$  and over, when the action was quite

rapid, the respective chlorides subliming and condensing in the cooler portion of the tube beyond.

The metals used in these experiments were not specially purified, but were such as are furnished by the best German manufacturers as pure.

CHEMICAL LABORATORY,  
VANDERBILT UNIVERSITY, JULY, 1893.

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### THE ELECTRO-DEPOSITION OF IRIIDIUM; A METHOD OF MAINTAINING THE UNIFORM COMPOSITION OF AN ELECTROPLATING BATH WITHOUT THE USE OF AN ANODE.<sup>1</sup>

BY WM. L. DUDLEY.

**I**N 1884 while engaged in studying the metallurgy of iridium from a commercial standpoint, I made many experiments in order to obtain a satisfactory bath for the electro-deposition of the metal. From a practical standpoint many difficulties were encountered, while experimentally most solutions of iridium yield the metal very readily under the influence of the electric current.

Much experimenting was done with the hope that a method might be devised by which a solution of the metal could be obtained electrolytically, thus avoiding the tedious and expensive processes for dissolving the platinum metals, but without success. Many electrolytes were employed under all conceivable conditions with iridium anodes in various forms, especially plates made by fusing iridium with phosphorus, but nothing practical was obtained. The iridium solutions were therefore made by several of the well known methods.

The next problem to be solved was to keep the solution of constant metallic strength and purity. Every electro-metallurgist knows that a plating bath must remain constant in composition, and that the slightest change in any particular will impair its

<sup>1</sup> Read before the American Association for the Advancement of Science, Madison Meeting, August, 1893.

working qualities when once the conditions for the best results have been attained. Ordinarily the uniform composition of the bath is maintained by using an anode of the pure metal which is being deposited. In the case of iridium this method of enriching the bath was hopeless, judging from previous experiment.

It was soon apparent that an iridium bath could be maintained of uniform metallic strength and composition in two ways only—(1) by an oxide and (2) by a hydroxide; and further, that the oxide or hydroxide used must be insoluble in the electrolyte but readily soluble in the acid radicle set free at the anode. Thus this part of the problem was solved and for various reasons the iridic hydrate,  $\text{Ir}(\text{OH})_3$ , was employed. The precipitated hydrate could be suspended in the bath at intervals by stirring, and the excess be allowed to settle before using; the liberated acid would thus be neutralized. But in practice it was found best to use carbon plates as anodes and to surround each plate with a loose fitting linen bag containing the  $\text{Ir}(\text{OH})_3$ . By this means the acid is neutralized soon after liberation and before it can diffuse through the solution. Thus the bath is kept uniform and clear. Bags containing the hydrate can be hung into the solution at other points if found desirable.

Various salts were found to give very good results, and I may mention the sodium iridichloride, the ammonium iridichloride, and a solution made by dissolving the hydrate in sulphuric acid and adding ammonium sulphate.

Like all hard and brittle metals the electro deposit has a tendency to blister and considerable care in the regulation of the current-strength is necessary.

At the time this work was being carried on, it was thought that the plan of using the hydrate to keep up the metallic strength of a plating bath would find wider application, and be useful in solving the problem of aluminum plating should a suitable bath for the deposition of that metal be discovered. The cheap production of the metal, however, has solved this problem independently.

In May, 1890, my friend Dr. Wm. H. Wahl, secretary of the Franklin Institute, wrote, saying that he was revising his work on "Galvano-Plastic Manipulation," and asking me to furnish

him some details of the iridium plating process. I sent him an outline of the method, describing the use of the iridium hydrate in lieu of a soluble anode. He replied at once that I anticipated him inasmuch as he had just worked out the same plan to solve the platinum plating problem after a year of hard labor. It was a source of great regret to us both for in neither case had the method been devised without much thought and labor, although it is so simple. Dr. Wahl read his paper on platinum plating before the chemical section of the Franklin Institute, on May 20, 1890, in which he made generous mention of my work. I regret that I could not have saved him so much labor; but owing to my relations to the corporation for which I was making the investigations, I have been unable to publish the results sooner.

CHEMICAL LABORATORY,  
VANDERBILT UNIVERSITY,  
July, 1893.

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## ALUMINUM.

BY R. L. PACKARD.

(Continued from page 236.)

*Metallurgical use.*—The quantity of aluminum used in this country in the manufacture of iron and steel castings is probably from twenty-five to thirty per cent. of the total production. In Europe it is estimated by Professor Wedding to be fifty-four per cent. This use, as was explained in the last number of this series, consists in adding from 0.10–0.15 per cent. of aluminum to iron or steel just before casting, by which blow-holes are prevented and sounder castings are produced. This use is becoming general. The beneficial effect, as was shown by experiments referred to last year, is due in part at least to the deoxidizing action of aluminum upon carbon monoxide at a high temperature, a reaction which was demonstrated directly between the metal and the gas. This subject has not yet received an exhaustive examination. For this purpose it would be necessary to know the composition of the iron or steel operated on in each case and make comparative tests on the different specimens. It is also probable that the method of melting employed has an effect on the result.

A detail of manipulation in the method of applying aluminum, especially in casting for steam and pump cylinders and other castings intended to resist high pressures, is reported in *Dingler's poly. J.*, (284, No. 11, 255). The addition is made by first forming a mixture of aluminum and iron, which is effected by placing the proper quantity of heated aluminum in the bottom of a small ladle, running some iron into the ladle from the furnace, and waiting until the mixture begins to stiffen. Then the iron to be operated on is run into a large ladle and the iron-aluminum mixture is poured into it, whereby an intimate mixture of the whole is effected. For 100 kilograms of iron to be operated on 200 grams of aluminum are used ( $= 0.20$  per cent.). The iron is not poured at once from the large ladle, but is allowed to stand until it is orange-yellow and a thin film begins to form on the surface. As soon as this occurs the film is removed and the iron is poured. The mold should be kept full. No reason is assigned for this procedure, but it appears that iron containing aluminum is inclined to shrink excessively and that this tendency must be obviated by pouring as cold as possible.

According to a paper read by Mr. J. W. Langley, at the Glen Summit meeting of the American Institute of Mining Engineers, the practice in the United States in pouring ingots is as follows: The aluminum, in small pieces of one-fourth or one-half pound weight, is thrown into the ladle during the tapping, shortly after a small quantity of steel has already entered it. The aluminum melts almost instantaneously and diffuses with great rapidity throughout the contents of the ladle. The diffusion seems to be complete, for the writer had never seen the slightest action indicating want of homogeneity of mixture, all of the ingots poured from one ladle being precisely alike so far as the specific action of the aluminum was concerned. The quantity of aluminum to be employed will vary slightly according to the kind of steel and the results to be attained. For open-hearth steel, containing less than 0.50 per cent. carbon, the amount will range from five to ten ounces per ton of steel. For Bessemer steel the quantities should be slightly increased, *viz.*, seven to sixteen ounces. For steel containing over 0.50 per cent. carbon, aluminum



should be used cautiously; in general between four and eight ounces to the ton. If these statements are put in the form of percentages, it will at once be seen how extremely minute is the quantity of aluminum which causes such marvelous results, for the numbers are:

4 ounces = 0.0125 per cent. ....	= 1-8000
5 ounces = 0.0156 per cent. ....	= 1-6500
8 ounces = 0.0250 per cent. ....	= 1-4000
16 ounces = 0.0500 per cent. ....	= 1-2000

*Soldering.*—From the articles which occasionally appear in the trade journals, both in this country and in Europe, and the patent list, it appears that the difficulties of soldering aluminum have not been overcome. Some of the new solders are introduced here without comment.

Chloride of silver has been recommended as a solder. It is to be finely powdered and spread along the junction to be soldered and melted with the blow-pipe. Mr. Joseph W. Richards makes an alloy of aluminum one part, zinc eight parts, tin thirty-two parts, and phosphor-tin, containing five per cent. phosphorus, one part. The aluminum is first melted, then the zinc is added, and finally the tin, which has been melted separately and mixed with the phosphor-tin. The alloy is poured into small bars for use. The object is to provide in the phosphorus a powerful reducing agent to prevent the formation of the film of oxide which usually prevents the intimate contact of the opposed surfaces. (United States patent 407,789, October 5, 1891.) Another formula is, cadmium fifty parts, zinc twenty, tin thirty. The zinc is first melted, then the cadmium is added, and finally the tin (*Dingler's poly. J.*, **284**, No. 6, 144). Electroplating the surfaces with copper and then applying the solder was mentioned last year.

Other solders which have been used are composed of:


	I.	II.	III.	IV.	V.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Aluminum .....	12	9	7	6	4
Copper .....	8	6	5	4	2
Zinc .....	80	85	88	90	94

In making these solders the copper should be melted first, the aluminum then added, and the zinc last. Stearin is used as a flux to prevent the rapid oxidation of the zinc. When the last

metal is fused, which takes place very quickly, the operation should be finished as rapidly as possible by stirring the mass, and the alloy should then be poured into an ingot mold of iron, previously rubbed with fat. The pieces to be soldered should first be cleaned thoroughly and roughened with a file and the solder placed on the parts in small fragments, the pieces being supported on a piece of charcoal. The place of juncture should then be heated with the blast lamp. The union is facilitated by the use of a soldering tool of aluminum. This last is said to be essential to the success of the operation. Alloy I is recommended for small objects of jewelry; alloy IV is said to be best adapted for larger objects and for general work, and is that most generally used. The successful performance of the act of soldering appears to require skill and experience, but the results obtained are said to leave nothing to be desired. Soldering tools of copper or brass should be avoided, as they would form colored alloys with the aluminum and solder. The skillful use of the aluminum tool, however, requires some practice. At the instant of fusion the operator must apply some friction, and, as the solder melts very suddenly, the right moment for this manipulation may be lost unless the workman is experienced.

*Alloys.*—It is regretted that no statistics of the production of aluminum bronze and ferro-aluminum in this country can be given for 1891. Both of these valuable alloys have been produced by the Cowles Electric Smelting and Aluminum Company for a number of years, and have found their way into the market on a considerable scale. The ferro-aluminum made by this company was used as a vehicle for adding aluminum to iron and steel in making sound castings when that method was first introduced. Aluminum bronze is coming into use in Germany for torpedoes on account of its strength and non-corrodibility, and for telephone wires. It was estimated that 280,000 kilograms would be used during 1892. The five per cent. bronze has been used for some time for nozzles of gas motors on account of its non-oxidizable character, and the twelve per cent. bronze is used for the pins of needle guns, for which purpose it is said to be better than steel.

The number of patents which have been granted for aluminum



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alloys, either where that metal forms a minor ingredient or has small quantities of other metals added to it for special purposes, shows that experimenting in this direction is increasing. As yet much of this experimenting is done without definite knowledge or aim on the part of inventors. Doubtless, in time, valuable conclusions may be derived from this kind of work, after rigid experiments with a definite purpose or idea have been undertaken. Of alloys formed with a specific purpose in view, that containing a small quantity of titanium, and another containing silver, were described last year. Others are mentioned in a lecture by Mr. Hunt, president of the Pittsburg Reduction Company, whose statements are valuable because they are based on knowledge and experience. He says :

“ The alloys of from two and one-half to twelve per cent. aluminum with copper have so far achieved the greatest reputation. With the use of eight per cent. to twelve per cent. aluminum in copper we obtain one of the most dense, finest-grained, and strongest metals known, having remarkable ductility as compared with its tensile strength. A ten per cent. aluminum bronze can be made in forged bars with 100,000 pounds tensile strength, 60,000 pounds elastic limit, and with at least ten per cent. elongation in eight inches. An aluminum bronze can be made to fill a specification of 130,000 pounds tensile strength and five per cent. elongation in eight inches. Such bronzes have a specific gravity of about 7.50, and are of a light yellow color. For cylinders to withstand high pressures such bronze is probably the best metal yet known.

“ The five to seven per cent. aluminum bronzes have a specific gravity of 8.30 to 8, and are of a handsome yellow color, with a tensile strength of from 70,000 to 80,000 pounds per square inch, an elastic limit of 40,000 pounds per square inch. It will probably be bronzes of this latter character that will be most used, and the fact that such bronzes can be rolled and hammered at a red heat with proper precautions will add greatly to their use. Metal of this character can be worked in almost every way that steel can, and has for its advantages its greater strength and ductility, and greater power to withstand corrosion, besides its fine color. With the price of aluminum reduced only a very

little from the present rates, there is a strong probability of aluminum bronze replacing brass very largely.

"A small percentage of aluminum added to Babbitt metal gives very superior results over the ordinary Babbitt metal. It has been found that the influence of the aluminum upon the ordinary tin-antimony-copper Babbitt is to very considerably increase the durability and wearing properties of the alloy. Under compressive strain aluminum Babbitt proves a little softer than the ordinary Babbitt. A sample one and one-half inches in diameter by one and one-half high began to lose shape at a pressure of 12,000 pounds. A similar sample of the same Babbitt metal without the addition of the aluminum (having a composition of 7.3 per cent. antimony, 3.7 per cent. copper, and eighty-nine per cent. tin) did not begin to lose its shape until a compressive strain of 16,000 pounds had been applied. Both samples have stood an equal strain of 35,000 pounds. In comparative tests of the ordinary Babbitt metal and the aluminum Babbitt metal, the latter has given very satisfactory results.

"The following alloys have recently been found useful: Nickel-aluminum, composed of twenty parts nickel and eight parts aluminum, used for decorative purposes; rosine, composed of forty parts nickel, ten parts of silver, thirty parts aluminum, and twenty parts tin, for jewelers' work; sun bronze, composed of sixty parts cobalt (or forty parts cobalt), ten parts aluminum, forty (or thirty) parts copper; metalline, composed of thirty-five parts cobalt, twenty-five parts aluminum, ten parts iron, and thirty parts copper.

"Prof. Roberts Austin has discovered a beautiful alloy containing twenty-two per cent. aluminum and seventy-eight per cent. gold, having a rich purple color, with ruby tints.

"The addition of from five per cent. to fifteen per cent. aluminum to type metal composed of twenty-five per cent. antimony and seventy-five per cent. lead makes a metal giving sharper castings and a much more durable type."

Mr. A. H. Cowles makes an alloy for electrical purposes consisting of manganese eighteen parts, aluminum 1.2 parts, silicon five parts, zinc thirteen parts, and copper 67.5 parts. This alloy has a tensile strength of 26,000 kilograms and twenty per cent.

elongation. Its electric resistance is greater than that of "neusilber," and it is therefore especially applicable for rheostats. (*Chemiker-Zeitung*, March 12, 1892.)

Mr. C. C. Carroll makes an aluminum alloy for dentists' fillings, consisting of silver 42.3 per cent., tin fifty-two per cent., copper 4.7, and aluminum one per cent. It is reduced to powder and then forms an amalgam with mercury. (U. S. patent 475,382, May 24, 1892.)

Mr. Chas. B. Miller has patented an anti-friction alloy of lead 320 parts, antimony sixty-four, tin twenty-four, aluminum two. (U. S. patent 456,898, July 28, 1891.)

Mr. Thomas MacKellar has patented an alloy for type metal of lead sixty-five parts, antimony twenty, and ten parts of an alloy consisting of equal parts of tin, copper, and aluminum. The tin-copper-aluminum alloy is first melted, the antimony added to it, and the mixture is then added to the melted lead. (U. S. patent 463,427, November 11, 1891.)

An aluminum bronze alloy contains aluminum twelve to twenty-five parts, manganese two to five, copper seventy-five to eighty-five. It is the product of John A. Jeancon. (U. S. patent 446,351, February 10, 1891.)

The anti-friction metal (Babbitt metal plus aluminum) contains antimony 7.3 parts, tin eighty-nine, copper 3.7, with from  $\frac{1}{4}$  to 2.5 parts of aluminum. It is patented by Alexander W. Cadman. (U. S. patent 464,147, December 1, 1891.)

*Aluminum imported and entered for consumption in the United States from 1870 to 1891.*

Years ending	Quantity, pounds.	Value.	Years ending	Quantity, pounds.	Value.
June 30, 1870.....	.....	\$ 98	June 30, 1882.....	566.50	\$ 6,459
" " 1871.....	.....	341	" " 1883.....	426.25	5,079
" " 1873.....	2.00	2	" " 1884.....	595.00	8,416
" " 1874.....	683.00	2,125	" " 1885.....	439.00	4,736
" " 1875.....	434.00	1,355	Dec. 31, 1886.....	452.10	5,369
" " 1876.....	139.00	1,412	" " 1887.....	1,260.00	12,119
" " 1877.....	131.00	1,551	" " 1888.....	1,348.53	14,086
" " 1878.....	251.00	2,978	" " 1889.....	998.00	4,840
" " 1879.....	284.44	3,423	" " 1890.....	2,051.00	7,062
" " 1880.....	340.75	4,042	" " 1891.....	3,906.00	6,263
" " 1881.....	517.10	6,071			

## IRON AND STEEL.

EDITED BY P. W. SHIMER.

### CARBON IN STEEL.

**I**N *Zeitschrift für angewandte Chemie*, 1893, parts 11, 13, and 14, Dr. Richard Lorenz gives some remarkable results obtained by him in the determination of carbon in steel by different methods. The conclusion is reached that the method by volatilization in a current of chlorine, the double chloride of copper and ammonium method, the copper sulphate method, and the chromic acid method yield results that are below the truth. A direct oxidation method devised by the author gives higher results which are supposed to be more nearly correct.

As to the chlorine method the conclusions are as follows: When the ignition in chlorine is prolonged beyond the point of complete volatilization of the ferric chloride, carbon goes off in combination with chlorine. When the ignition is interrupted before this point is reached, some iron carbides remain undecomposed and these are not completely oxidized in the subsequent combustion in oxygen. Even when the ignition is interrupted at the proper point, the results are low.

The conclusions as to the action of cupric ammonium chloride solution on steel are the following: 1. The reaction, which apparently is very rapid, is really, in its last stages, at the ordinary temperature, quite slow, and often requires many days to complete it. 2. On account of the presence of chlorine in the carbonaceous residue it is necessary to burn it in a tube containing lead chromate instead of the usual copper oxide. 3. By too long standing in contact with the copper solution a part of the carbon is lost either by solution or by a gradual throwing off of gaseous hydrocarbons. The series of carbon results obtained by allowing the copper solution to act on samples of steel borings from sixteen hours to ten days show an increase of carbon to a maximum (usually after several days) and then a decrease, owing to loss of carbon by long standing in the copper solution. The higher results are supposed to be more nearly correct. By use of a neutral copper sulphate solution the carbon results obtained



were much lower than when the solution of the double salt was used. This was plainly due to loss of gaseous hydrocarbons.

In the standard method proposed by the author he weighs from two to four grams of steel into a porcelain boat and covers the sample with a layer of powdered fused lead chromate. The boat is pushed into a porcelain tube and heated to a white heat in a specially constructed combustion furnace provided with blast of air. From thirty to forty minutes are required to complete a determination. A few of the more important determinations are the following :

	A	B	C	D
Carbon (average, by author's method) .....	0.63	0.74	1.00	1.05
Carbon (maximum, by double chloride method) ..	0.63	0.72	0.96	0.99

For the determination of carbon in chrome steel, ferro-chrome and manganese the method seems to give higher and probably more trustworthy figures than the methods heretofore used.

In his work with the double chloride of copper and ammonium solution the author seems to have failed to profit by the work of the American committee on international standards. If his double chloride solutions had been absolutely free from carbonaceous matter and had been strongly acidified with hydrochloric acid as the committee found essential, it is probable that the results would have agreed closely with those obtained by his ingeniously devised direct combustion method.

## GERMAN ECONOMY IN IRON MANUFACTURE.<sup>1</sup>

BY FRANK H. MASON, CONSUL-GENERAL.

IT has been recently noted in England with something like alarm that the production and export trade of iron and steel in Germany have been steadily growing during the past ten years at a rate out of all proportion to the development of Great Britain in the same field, and that railway wheels, ties, axles, wire, etc., of German origin are not only making serious inroads upon foreign markets which British exporters have hitherto almost exclusively controlled, but are now sold to some extent in England. The fact that, in spite of all advantages which English ironmasters derive from long experience, cheap and abundant

<sup>1</sup> *Consular Reports*, No. 155, August, 1893.

coal, and unequaled shipping facilities, they are now undersold on their own ground by their German rivals would seem incredible if it were not sustained by actual statistics; and it may be of interest to American metal workers to examine briefly the more obvious causes of the notable progress of Germany in this important branch of industry.

It is conceded that until about 1880 the British export trade in iron and steel was all that could be reasonably desired. Not only in respect to coal and skilled labor, but in facilities for importing ores from Spain, Scandinavia, and other foreign sources and for exporting their product, the English and Welsh furnace men seemed to have a secure advantage over their continental rivals. But it is now found that English exports of railway iron and steel have fallen from 1,000,000 tons per annum a few years ago to 703,370 tons in 1891 and 467,986 tons in 1892, while German exports of the same products, which had scarcely begun in 1880, have risen to 198,421 tons in 1890 and 233,943 tons in 1891, with a total export of pig and finished iron and steel amounting to a yearly average of 1,050,000 tons. Not only this, but, in spite of the increased cost of coal in Germany, due to higher wages demanded by miners and the steadily increasing coal consumption in face of a definitely limited supply, the metal production of Germany has continued to increase. The proportions of this growth will be apparent when, with the fact in mind that in 1870 the total output of Germany was only 886,000 tons of iron and 125,000 tons of steel, we consider the following statistics of finished iron and steel manufacture in this country during the past two years:

Description.	Tons, 1891.	Tons, 1892.
Bar and section iron.....	1,335,000	1,334,000
Blooms, billets, and ingots .....	690,700	790,500
Plates.....	417,500	425,100
Tin plates.....	21,300	23,400
Steel and iron rails.....	824,800	891,400
Wire.....	339,200	402,500
War materials.....	10,100	11,100
Total .....	3,638,600	3,878,000

The increase in 1892, it will be seen, was 239,400 tons.

Comparing the growth of iron and steel production in Great Britain and Germany from 1880 to 1892, inclusive, it appears

that, whereas England shows an increase of only seventy per cent., Germany has achieved during the same period a net growth of nearly or quite 400 per cent.

A result as striking as this must be the outgrowth of causes so radical as to be interesting to all who are concerned, either theoretically or commercially, in the metallurgy of steel and iron. The growing importance of Germany in this field would seem to be due largely to two fundamental facts: (1) The introduction of the basic process, which enables the iron and steel makers of Westphalia, Silesia, and the Saarbrück district to use their cheap and abundant native ores; and (2) the unrivaled chemical skill of the Germans whereby they have succeeded in saving the by-products of coke manufacture, thus deriving a revenue from processes which in other countries entail a waste of material and financial loss.

#### THE BASIC PROCESS.

Of the basic process itself there is little or nothing new to be said. It is understood as fully and practiced as successfully in the United States as in any part of the world. But its introduction into Germany has revolutionized the whole economy of steel manufacture in this country. With fair facilities for importing the richer ores of Spain and Sweden, the German furnace men found their whole list of native ores available, and when special processes were necessary to facilitate the employment of materials which had previously been considered worthless, they were invented and applied. In a previous report of this series (No. 137, p. 246) an account was given of a special process for the desulphuration of raw iron from the blast furnace by treatment with manganese, as invented and first practiced in direct steel production at Hörde, in Westphalia. This process, which has since been adopted at various other points on the Continent and in England, secures the production of excellent steel from materials so heavily charged with sulphur as to be impracticable for that purpose by ordinary methods.

#### ECONOMY OF BY-PRODUCTS OF COKE.

Equally original and not less important to the general economy of iron manufacture are the more recent German improvements in coke making, by which the subsidiary products—ammonia,

tar, and tar oils, with their valuable elements benzene, anthracene, etc.—are saved from the waste that attends the ordinary coking process. In this special field Germany is now so far in advance of other countries that some understanding of the methods employed here is important in the present connection.

The first record of any practical interest in the saving of ammonia and tar from the coking process appears in a paper which was read before a convention of ironmasters at Dusseldorf by one F. W. Lurman in 1858. The main principles involved were clearly stated, but the requisite apparatus was so elaborate and expensive and the financial results then so doubtful that progress was for a long time slow and uncertain. The improved methods now in use, and which have produced the best results, are mainly the work of the past five years. What is known as the Semet-Solvay system is the one principally in use in Belgium; but the most advanced representative of German progress in this direction is probably the Otto-Hoffman coke oven, of which there are about 1,550 now in use—535 in Westphalia, 700 in Silesia, seventy-five in the Saar district, and 240 in Austria. Although elaborate and costly in construction, this oven is durable and, by reason of its great saving in gas, highly economical in operation, aside from its efficiency in saving the subsidiary products. The complete apparatus is a combination of the Otto oven (thirty-two feet long, sixteen inches wide, and five and one-half feet high) with the Siemens regenerator in such manner that the air to be used for the combustion of gases is first heated to a temperature of about 1800° F.

For the most economical service these ovens are built in groups or batteries of sixty, and half the number are alternately filled each forty-eight hours. The oven has three openings through which it is charged from above with six and one-half tons of air-dried coal. The openings being then tightly closed, heat is applied, and the gases generated are drawn off through collecting pipes by the action of a suction fan into coolers and scrubbers, where the tar and ammonia are deposited in water by mechanical distillation. The gas, thus purified of tar and ammonia, is then reconducted to the bottom of the ovens, where it is mingled with the heated air above mentioned and burned as

fuel in the process of roasting the coal. The percentage of gas produced varies somewhat with the quality of coal used ; but with all the German coals the gas thus generated is greatly in excess of what is required for heating the ovens, and the surplus is available for making steam, lighting, and for other purposes.

The water from the coolers and scrubbers, charged with the ammonia that has been absorbed from the gas, is subjected to heat, which expels the ammonia as vapor, which in presence of sulphuric acid forms sulphate of ammonia, a white salt that is extensively used for fertilizing purposes. The tar, by reason of its gravity, settles to the bottom of the water and is easily separated. It is more valuable than the tar produced in the ordinary manufacture of illuminating gas, on account of its greater percentage of benzene and anthracene. For a long time there prevailed among German ironmasters a notion that coke produced by any process that saved the by-products was thereby injured for iron-making, but this is now completely dispelled. The coke made by the above process is conceded to be of the highest quality for all purposes.

The operation of coking requires in the Otto-Hoffman ovens from twenty-four to forty-eight hours ; and the product from good air-dried coal containing from fifteen to seventeen per cent. of water is about seventy-six per cent. of coke, 1.15 to 1.25 per cent. of sulphate of ammonia, and from 2.5 to 4 per cent. of tar. In a recent number of the *Journal für Gasbeleuchtung und Wasserversorgung* (Munich) the following résumé is given of the actual work of a battery of sixty ovens, operating with local coal in the three principal mining districts of Germany.

One ton of coal produces :

District.	Coke. Pounds.	Tar. Pounds.	Sulphate of ammonia. Pounds.
Ruhr .....	1,672	60.5	25.3
Silesia .....	1,496	93.5	26.4
Saar .....	1,540	91.3	18.7

The yearly product of sixty ovens is :

District.	Coke. Tons.	Tar. Tons.	Sulphate of ammonia. Tons.
Ruhr.....	51,300	1,860	780
Silesia.....	48,000	3,000	840
Saar.....	40,500	2,400	492

The generation, consumption, and surplus of gas for one oven per day are as follows :

District.	Production. Cubic feet.	Consumption. Cubic feet.	Surplus. Cubic feet.
Ruhr .....	32,000	19,200	12,800
Upper Silesia .....	36,800	20,800	16,000
Saar .....	32,000	19,200	12,800

So that a battery of sixty ovens, working under the above conditions, would furnish gas for their own heating and yield a surplus of from 76,000 to 96,000 cubic feet per day to be used for other purposes. It is reckoned in practice that 100 cubic meters (3,200 cubic feet) of this surplus coke gas is equivalent, for purposes of heating, to 87.5 kilograms (193.5 pounds) of coal; and the saving of fuel in working sixty coke ovens would therefore be :

District.	Per day. Kilograms.	Per year. Tons.
Ruhr .....	21,000	7,560
Silesia .....	26,250	9,450
Saar .....	21,000	7,560

But, since the Otto-Hoffman oven involves, also, the use of the other appliances which require heat to the extent of one-third the amount saved in the form of gas, it follows that the actual economy in fuel is about two-thirds of the above totals expressed in coal. Add to this saving of coal the two by-products—sulphate of ammonia, worth in the market \$5.23 per 100 kilograms (220 pounds), and tar, worth about ninety-five cents per 100 kilograms—and the enormous profits which are claimed for this system do not appear incredible.

From another, but trustworthy, source it is announced that the revenue actually derived from the tar and ammonia produced by one year's working of a group of sixty ovens in Westphalia, which cost in construction \$166,000 (or \$2,766 each), was \$40,200, or about twenty-five per cent. on the capital invested in the plant. The price given above does not include the cost of condensing apparatus, which, although it is not a part of the oven, is worked in connection with it.

It should not be understood from the foregoing that the Otto-Hoffman is the only highly improved coke oven in Germany which saves the secondary products. There are, in fact, several others

of later construction for which their inventors claim certain points of superiority over the Otto, but the latter has been longest in use and is therefore the best known. From the known aggregate product of tar and ammonia in this country, it is calculated that there are at present in operation in the country not less than 3,000 coke ovens which save the subsidiary products, so that the 1,550 Otto ovens in operation are something more than half the entire number of all kinds in actual use.

A comparison of the results obtained by the Semet-Solvay system in Belgium with those realized by the best German ovens shows a clear advantage in favor of the latter. In the Semet ovens an intense degree of heat is generated, so that it is not found necessary to combine them with regenerators to heat the air which is to be used in combustion. They are therefore considerably cheaper in construction; but, on the other hand, the Semet requires for good results a special mixture of "fat" and "lean" coal that is not always easy to provide, and, while the coke thus made is of a high and uniform quality, it produces much less ammonia, tar, and gas than the best German ovens, and is therefore in the end less profitable.

The direct production of benzene in the coking process is difficult, but it has been successfully accomplished during the past year by an inventor at Dortmund, whose process is thus far a secret. So far as can be ascertained, from six and one-half to fifteen pounds of benzene are obtained from a ton of dry coal; and, as benzene is an important element in anilin manufacture, it may be ranked among the products that will always have a standard value. The effect of the 3,000 improved coke ovens now in use in Germany and Austria has been to greatly increase the supply and reduce the market values of the by-products which they secure. Sulphate of ammonia, which, besides its uses as a fertilizer, is largely employed in making ice and in soda manufacture, was in 1883 worth \$7.37 per 100 kilograms, but now sells for about \$5.25; and tar has declined from \$1.30 per 100 kilograms to ninety-five cents in the same period. Notwithstanding this decline, the profits derived from these two subsidiary products of coke manufacture are stated by good authorities to be as high as forty per cent., all of which goes to

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the credit side in the general account of Germany's mining and metal industries.

But this is not all. Still another point in which the Germans secure an important advantage, especially as respects their American competitors, is in economizing the waste and coarser forms of fuel. It is conceded that Americans are masters of economy in labor, but they are extravagant with materials. In our country millions of tons of coal dust—the waste of mines, railways, and iron mills—are thrown away as useless. An official commission, after exhaustive study of the subject, has recently published the astounding information that for every ton of anthracite coal mined and marketed in Pennsylvania, one and one-half tons are wasted; and the loss in bituminous coal, although somewhat less, is still enormous. In Germany, France, and Belgium all this refuse coal dust is carefully saved. Part of it is mixed with pitch derived from tar distillation and molded into "bricquettes," which are used as fuel for locomotives, stationary engines, and household grates. The remainder of this finely pulverized carbon is blown by jets of live steam into various kinds of furnaces, where it burns with almost the fierceness of crude petroleum. Coal dust from mines costs in Germany twenty-five cents per ton on cars, or in large quantities \$2.38 per carload of ten tons, and the care with which it is saved and utilized adds an important percentage to the fuel supply of this country. It is by this application of scientific economy to every stage of manufacture, the saving of secondary products, and the invention of new processes and machinery to work most advantageously native materials that the German iron and steel makers have been able to face without disaster the declining metal markets of the past four years.

The question may be fairly asked whether the time has not come for Americans to study far more carefully than they have studied hitherto the scientific economies of manufacture. Europeans stand aghast at the recklessness with which our forests and mines and petroleum deposits are being exhausted and the soil of vast acres drained of its fertility by forms of culture which wring a yearly crop from the land, but give back little or nothing in return. There are in nearly every coal-mining dis-



tract in the United States great mounds and embankments of discarded slack and coal dust which, under a better system, might be utilized as fuel; and fortunes are lost every year in the clouds of gas and smoke that rise from the coke ovens of Virginia, Pennsylvania, Ohio, and Alabama. With soda, salt, and phosphate beds in a dozen states, we import the heavy chemicals for soap and paper making and annually purchase from Europe sulphuric acids and chemical fertilizers which ought to be made at home. There is a lesson in the coke ovens and chemical laboratories of France and Germany which the economists and manufacturers of America can not study too thoroughly nor too soon.

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### NEW BOOKS.

RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES. BY FRANCIS C. PHILLIPS.<sup>1</sup>

The dissertation, which is reprinted from the *Transactions of the American Philosophical Society*, 17, May 26, 1893, is published in two parts, the first of which deals with:

(a) Phenomena of Oxidation of Hydrogen, Carbonic Oxide, Gaseous Paraffins, Olefines, and Acetylene.

(b) Qualitative Reactions of Gases.

(c) Substitution Products of the Action of Chlorine Upon Methane.

(d) Preparation of Halogen Compounds of Alkyls and Olefines.

In (a) the author has directed his experiments chiefly towards ascertaining the temperatures at which combustible gases, when mixed with air and passed over asbestos impregnated with various metals, will unite with oxygen. Asbestos fiber was coated with the different metals by moistening the asbestos with a solution of the chloride of the metal and then dropping alcohol on the fiber and igniting it. The metals employed were palladium, gold, platinum, iridium, osmium, rhodium, and palladium-platinum. About 0.3 gram of the asbestos thus prepared

<sup>1</sup> Dissertation for the degree of Doctor of Philosophy, University of Pennsylvania.

was placed in a glass tube of one-eighth inch bore, and this tube was heated in an iron oven, the lower portion of which was filled to the level of the glass tube with iron turnings. A thermometer inserted into the turnings gave the temperature. Above 300° the temperature was approximately determined by inserting into the iron turnings glass tubes containing small amounts of different salts of known melting points.

In the experiments upon the oxidation temperatures of the hydrocarbons, air containing a small measured percentage of the hydrocarbon was freed from carbon dioxide by shaking with caustic soda solution, then dried by sulphuric acid, and the gas mixture was then passed through the glass tube. The formation of water was detected by inserting in the farther end of the glass tube a mixture of crystallized ferrous sulphate and potassium ferricyanide, the salts being ground separately and mixed just before using. Carbon dioxide was detected by passing the escaping gases through lime water.

The gases whose behavior under the above conditions was investigated were hydrogen, methane, ethane, propane, isobutane, pentane, heptane, ethylene, propylene, trimethylene, isobutylene, acetylene, benzene, alcohol vapor, and carbon monoxide. The gases were carefully prepared and purified, but it does not appear that the author assured himself of their purity by quantitative analyses.

The author states the results of this group of experiments as follows:

"1. The temperature of oxidation is mainly dependent upon the solid bodies with which the gas is in contact.

"2. Two phases are often, but not always, to be observed in the process of oxidation. As the temperature rises a point is reached at which a minute and scarcely recognizable trace of carbon dioxide appears. After the slow oxidation has continued for some time and gradually increased during a rise of temperature of twenty, thirty, or even more degrees, a sudden intense reaction occurs in the lime water. \* \* \* Very often this slow oxidation is not observed and the carbon dioxide reaction occurs in the lime water suddenly and with full intensity. \* \* \*

"3. The oxidation of a hydrocarbon by air, under conditions similar in all respects, does not occur always at the same temperature. \* \* \* A variation in the proportion of hydrocarbon and air does not seem to materially influence the oxidation temperature.

"4. The paraffins are the most stable towards heated air in presence of palladium. Acetylene and carbonic oxide stand next in order. The olefines are the most easily oxidized.

"5. Of the members of the same homologous series of hydrocarbons, the lower are the more stable towards oxidizing influences.

"6. Hydrogen stands alone among combustible gases in undergoing oxidation under the influence of palladium-coated asbestos in the cold.

"7. Oxidation of gaseous hydrocarbon in excess of air involves the simultaneous formation of carbon dioxide and water.

"8. In all cases where air is in excess, oxidation is complete (*i. e.*, yielding only carbon dioxide and water), even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, carbon dioxide may be partly replaced by carbon monoxide among the products of oxidation.

"9. As regards oxidizing power, the metals which I have studied might be arranged in the following order, beginning with the most active: (1) osmium, (2) palladium, (3) platinum, ruthenium, (4) iridium, (5) rhodium, (6) gold.

"10. At a bright red heat and in excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper.

"11. Glowing of the palladium is by no means essential to slow oxidation. \* \* \*

"12. The proportion of finely divided metal used upon asbestos seems to be immaterial. Palladium asbestos containing two per cent. of palladium is nearly as efficient as that containing thirty per cent."

In (*b*), part 1, are given the qualitative reactions of a number of gases upon various reagents in solution, and upon reagents used in solid form and heated to any desired temperature. The gases investigated are hydrogen, methane, ethane, propane,

isobutane, heptane, ethylene, propylene, isobutylene, trimethylene, carbon monoxide, acetylene, allylene, carbon oxysulphide, methyl hydrosulphide, methyl sulphide, nitrogen, and oxygen, and the action of carbon monoxide upon methane at high temperatures is tested. As the experiments do not admit of being given in condensed form, the reader must be referred to the original for details. Mention may, however, be made of a delicate reaction for hydrogen, which, according to the author, will detect one-twentieth of one per cent. of hydrogen in a neutral gas. It consists in passing the dry gas mixture over dry, cold, palladious chloride. The salt is decomposed with the evolution of hydrochloric acid, which is detected by passing it into dilute silver nitrate solution.

(c), part 1, contains a brief description of results obtained by passing a mixture of chlorine and methane through a heated combustion tube filled with bone black. The chief products seemed to be methyl chloride and tetrachlormethane, only small amounts of dichlormethane and chloroform being formed.

In (d), part 1, the preparation of halogen compounds of alkyls and olefines, and the literature of the subject are briefly discussed.

Part 2 is divided into :

(a) The Composition of Natural Gas as Found in Western Pennsylvania and Other Regions.

(b) A Method for the Quantitative Analysis of Natural Gas.

(c) The Origin of Natural Gas and Petroleum.

In this last the different theories are considered in considerable detail, the author differing from Engler and Mendeleeff, and upholding the theory of vegetable decomposition.

L. M. DENNIS.

## PROCEEDINGS.

### MINUTES OF THE COUNCIL OF THE AMERICAN CHEMICAL SOCIETY, 1893.

FEBRUARY 26, 1893.

The following is a copy of a communication received from H. W. Wiley, Washington, D. C. :

"We the undersigned respectfully petition the Board of Directors to incorporate the Washington Chemical Society as a local section of the American Chemical Society."

[SIGNED.]

H. W. Wiley,  
E. A. de Schweinitz,  
F. W. Clarke,  
Geo. Steiger,  
Charles E. Munroe,  
W. M. Mew,  
Robt. B. Warder.

Also a similar paper was received, signed by

Wm. H. Seaman,  
Jas. H. Griffin,  
Claude A. O. Rosell.

To the above application, the following was added :

"We the undersigned members of the council of the American Chemical Society, hereby request the Board of Directors to issue to the persons who have signed the above petition, a charter for the establishment of a local section of said society in the city of Washington, D. C."

[SIGNED.]

J. W. Mallet,  
A. B. Prescott,  
Alfred Springer,  
T. H. Norton,  
George F. Barker,  
Theodore G. Wormley,  
G. C. Caldwell,  
L. M. Norton,  
John Howard Appleton,  
C. F. Chandler,  
Albert C. Hale,<sup>1</sup>

<sup>1</sup> *Note.* As the constitution of the society does not provide for incorporating any other organization as a local section of the American Chemical Society, but merely for the formation of a local section "by the Board of Directors on receipt of a written request to that effect, signed by ten members of the society and endorsed by a majority of the council," the ten members above mentioned sent a new petition to the Board of Directors in conformity with the requirements of the constitution, and the Board of Directors thereupon issued to said ten members, under date May 10, 1893, a charter for the formation of a local section of the American Chemical Society in the city of Washington, D. C.

APRIL 12, 1893.

Prof. Edward Hart, Easton, Pa., was elected editor and third member of the Committee on Papers and Publications for the year 1893.

The following named persons were elected members of the society :

Cary, J. S., Chicago, Ill.  
Hoskins, Wm., Chicago, Ill.  
Heidenhain, H., Chicago, Ill.  
James, George, Chicago, Ill.  
Julian, Frank, South Chicago, Ill.  
Kennicott, C. L., Chicago, Ill.  
Liebmann, Adolph, Manchester, Eng.  
Low, W. H., Chicago, Ill.  
Puckner, W. A., Chicago, Ill.  
Sauer, H. E., Chicago, Ill.  
Stillwell, J. S., Prince's Bay, Staten Island, N. Y.  
Stuart, E. B., Chicago, Ill.  
Wickhorst, Max, Aurora, Ill.

APRIL 28, 1893.

The Committee on Papers and Publications, having received the following proposal, submitted it to the council, requesting them to approve or disapprove of making a contract with the Chemical Publishing Company in accordance with proposed terms. The council thereupon voted to approve a contract for an edition of seven hundred and fifty (750) copies at the rate of \$1.90 per volume in accordance with the terms of the proposal.<sup>1</sup>

## PROPOSAL.

Easton, Pa., April 17, 1893.

TO THE COMMITTEE ON PAPERS AND PUBLICATIONS, AMERICAN CHEMICAL SOCIETY.

Gentlemen :

We hereby propose to publish the Journal of the American Chemical Society, guaranteeing twelve (12) numbers per year, with a minimum of seven hundred and twenty (720) pages at the following rates :

For an edition of seven hundred and fifty (750) copies, at the rate of \$1.90 per volume ; for an edition of one thousand (1000) copies, at the rate of \$1.80 per volume. This includes wrapping, mailing, and everything in the way of expense of publication, except cuts, which the Society shall pay for at cost. When requested by the author at the time the

<sup>1</sup> *Note.* At a meeting of the Board of Directors of the American Chemical Society held June 8, 1893, a contract for 1000 volumes of the Journal was authorized upon the terms of the proposition submitted by the Chemical Publishing Company.

manuscript is submitted, twenty reprints will be furnished without cost ; a larger number than this will be charged for.

It is understood that we are to have the use of one advertising page for our own advertising exclusively without cost to either party.

We guarantee that the paper and typography and illustrations shall be in every respect equal to those of the current volume of the Journal of Analytical and Applied Chemistry.

Respectfully,

CHEMICAL PUBLISHING COMPANY,  
per Eugene C. Foster, Manager.

The following named persons were elected members of the society :

Andrews, Geo. F., Cornell and Andrews, Providence, R. I.  
Hewitt, Edward R., 13 Lexington Ave., New York City.  
Westessan, J. P. L., Navy Yard, Washington, D. C.  
Williams, Henry J., 161 Summit St., Boston, Mass.

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MAY 1, 1893.

Ordered by the council that the report of the general secretary on the condition of the American Chemical Society be printed for the information of members and others interested.

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MAY 27, 1893.

Dr. C. B. Dudley, of Altoona, Pa., was elected a member of the council for the remainder of the year 1893, to fill the vacancy caused by the death of Prof. L. M. Norton, of Boston, Mass.

Prof. Norton's death occurred April 26, 1893.

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JUNE 7, 1893.

The following named persons were elected members of the society :

Adamson, George P., Easton, Pa.  
Baker, John T., Easton, Pa.  
Baker, Haydn M., M. D., 27 Hart St., Brooklyn, N. Y.  
Clymer, Lee S., Hellertown, Pa.  
Crawley, J. T., Audubon Park, New Orleans, La.  
Daly, B., 813 Fifth St., N. W., Washington, D. C.  
Foster, Eugene C., Easton, Pa.  
Green, Charles B., Easton, Pa.  
Jones, Clemens, Easton, Pa.  
Lee, Fitzhugh, Easton, Pa.  
Peckitt, Leonard, Catasauqua, Pa.  
Shimer, Prof. Porter W., Easton, Pa.  
Scholl, George S., Catasauqua, Pa.,  
Wiborg, F. B., Clifton, Cincinnati, O.  
Westenhoff, John Hermann, 17 W. 3rd St., Cincinnati, O.

The following was adopted :

"Resolved that the general meeting of the American Chemical Society for the summer of 1893 be held in Chicago at such date as may be determined by the committee appointed by the society to arrange with the World's Fair Auxiliary of the Columbian Exposition for an International Congress of Chemists."

Some days later the decision of the committee was announced as follows :

474 Waverly Ave., Brooklyn, N. Y.,  
June 27, 1893.  
Prof. A. C. Hale,  
Sec'y American Chemical Society ;

Dear Sir :

The committee appointed to co-operate with the World's Congress Auxiliary, to whom was referred the time at which the general meeting of the society for the summer 1893 shall be held in Chicago, have determined upon August 21 as the date for the beginning, and that it shall be held in conjunction with the World's Congress of Chemists beginning on the same date.

Very respectfully,

Wm. McMurtrie,

Chairman committee to co-operate with the World's Congress Auxiliary.

JUNE 15, 1893.

The following proposition of Prof. Edward Hart, of Easton, Pa., submitted to the Council May 15, 1893, and to the Board of Directors June 8, 1893, and agreed to by that body on the last mentioned date, was approved by the Council June 15, 1893 :

"(a) That I suspend the publication of my Journal with the June number, and for the rest of the year send to my subscribers the numbers of the Journal of the American Chemical Society instead ; the expense of printing, binding, and mailing the additional copies required for this purpose to be defrayed by me. This plan gives my subscribers the society's journal for six months and will doubtless lead to a largely increased membership.

"(b) That in case the journal of the society shall at any time cease to be published by the Chemical Publishing Company, the American Chemical Society shall then, if I so desire, take all *complete volumes* of the Journal of Analytical Chemistry and of the Journal of Analytical and Applied Chemistry then in my hands, paying for them at the rate of one dollar (\$1) per volume, unbound. The total amount to be paid shall in no event exceed \$400. It is also understood that if additional copies of any number shall have been reprinted in the meantime, such additional copies shall not be included unless the society so desire."



JUNE 30, 1893.

The following named persons were elected members of the American Chemical Society:

Allen, Charles M., Pratt Institute, Brooklyn, N. Y.  
Becnel, Lézin A., McCall P. O., La.  
Bird, Maurice, Calhoun, La.  
Blonin, R. E., Baton Rouge, La.  
Bouton, Miss Rosa, P. O. Box 675, Lincoln, Neb.  
Brinker, H. L., P. O. Box 223, So. Bethlehem, Pa.  
Broberg, F. G. Abel, Landing, N. J.  
Buck, C. Austin, So. Bethlehem, Pa.  
Burney, W. B., Columbia, S. C.  
Chandler, Wm. Henry, So. Bethlehem, Pa.  
Davis, Wm. Walley, Roanoke, Va.  
Edson, Hubert, Patterson, La.  
Fulmer, Elton, P. O. Box 372, Lincoln, Neb.  
Hays, Joseph A., 147 S. 18th St., Pittsburg, Pa.  
Kiefer, Herman Eugene, So. Bethlehem, Pa.  
Landis, H. K., So. Bethlehem, Pa.  
Lee, J. G., N. La. Exp. Sta., Calhoun, La.  
Lehman, Adolph L. F., Audubon Park, New Orleans, La.  
Martin, Oscar W., Hughes High School, Cincinnati, O.  
McFarland, Chas. S., Burnside, La.  
Metz, A. L., Tulane Medical College, New Orleans, La.  
Morse, J. H., St. Patrick P. O., La.  
Richards, Joseph W., Bethlehem, Pa.  
Ross, B. B., Baton Rouge, La.  
Roussel, J. N., Audubon Park, New Orleans, La.  
Semple, Henry B. Jr., Easton, Pa.  
Shober, Niel B., So. Bethlehem, Pa.  
Smith, Ernest Ellsworth, 1104 Lexington Ave., N. Y.  
Spanutius, Fred. W., So. Bethlehem, Pa.  
Stubbs, W. C., Audubon Park, New Orleans, La.  
Townsend, Clinton P., Donaldsonville, Ascension Parish, La.  
Wyndham, Stanley, Ph.D., Judson, Florida.

The following named were elected associates:

McQuaid, W. M., Audubon Park, New Orleans, La.  
Robinson, L. W., Sugar Land P. O., Texas.  
Roth, David M., 36 Ingleside Pl., Cincinnati, O.

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# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

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## ADDRESS OF WELCOME TO THE WORLD'S CHEMICAL CONGRESS.

BY HARVEY W. WILEY, CHAIRMAN OF THE JOINT COMMITTEE OF ARRANGEMENTS AND  
PRESIDENT OF THE AMERICAN CHEMICAL SOCIETY.

Delivered Monday, August 21, 1893.

**G**ENTLEMEN: You have assembled here in response to the invitation of the World's Congress Auxiliary, tendered chiefly through the American Chemical Society, with the co-operation of the American Association for the Advancement of Science. On behalf of these organizations it becomes my pleasant duty to extend to you a cordial welcome.

The occasion of our meeting is no ordinary one. From the whole civilized world there have been collected in this city the fruits of man's inventive genius and of his industry. Accompanying these are the representatives of all nations, illustrating in their attire and villages the habits and customs of all countries. These varied collections and representatives reflect the life of all the continents and seas. With wondering eyes we have walked through Jackson Park, allured now by the masquerades of the Midway, and again by the palaces of the peristyle. Our eyes have been charmed by the aptly mingled colors of the painters, and bewildered by the brilliancy of the electric display. In hopeless wonder we have gazed at the broad acres of man's manufactures, engirdled by a gallery illustrating his appliances for education. The whole wealth of Ceres is lavishly portrayed in the palace of agriculture. By night the shore of the lake

and the borders of the South Pond are transformed into fairy scenes, more beautiful than the poet has ever pictured. The whole world of art, the whole world of work, and the whole world of skill are brought to us in a reality which, were it not so tangible, would seem the deception of a wizard.

For a week now we are called to leave this wonderful scene, the like of which has never before been revealed to the vision of men, for the purpose of studying for a time some of the aspects of one of those sciences which, still modest in its demeanor, has perhaps done more than any other to make the Jackson Park of to-day a possibility.

Illy suited for display, the science of chemistry is pleased to work to show the way to human progress, quite content to be forgotten when it is achieved. It asks for no white palace with imposing portals in which to display the wonders of its wealth. In odd nooks and corners, scattered over the vast expanse of space, attached to every other exhibit in an unobtrusive way, its silent work is revealed in countless combinations, the foundation of the arts. We may look in vain among the *bas-reliefs* for the names of Lavoisier, Priestley, Berzelius, Liebig, Hoffman, Lawrence Smith, Silliman or Chevreul, but the fruits of their labors may be found in almost every exhibit.

Chemistry is truly cosmopolitan. There is no one country that can claim it entirely, either by birth or adoption, Wurtz to the contrary notwithstanding. It is therefore entirely fit and proper that the chemists of all nations should now and then meet on common terms for the sake of mutually profiting by the advances and discoveries that each has made. I believe there will be brought before the present congress a proposal for the regular triennial meeting of the chemists of the world, after the plan which has been followed so successfully by our brethren the geologists and physicians. Were the object of such a congress only to listen to papers and addresses pertaining to the progress and development of our science, it might well be asked whether such conventions are useful. The chemical journals of to-day fully cover the whole field of chemical activity, and thus even in the most remote mining camp the chemist and assayer may be fully *en rapport* with his fellows the world over. But the

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objects of our congress are wider than the mere listening to papers. The chemist is a social being, and there is a life outside of the laboratory as beautiful and useful as the life within. The narrowness of an idea and the flattening of isolation are to be avoided as the purpose of an investigation is to be pursued. The highest culture is not found in books, but in men. The power and splendor of a great and old university are not alone in its libraries and professors. There is a subtle influence of association that does more, often, than the lecture room to develop mind and mold character. And thus to widen his horizon and broaden his views the chemist must leave his desk and seek the acquaintance of his fellows. Every time you take a brother chemist by the hand you enlarge your life and extend your strength, and the farther apart the field of your activities, the greater the benefit.

Dogmatism in science is no less reprehensible than dogmatism in theology, and yet many of us have seen samples of it. Believe if you will in a literal Adam, but for the sake of our science avoid that state which throws a saintly halo of supernatural splendor about a hypothetical sechseck.

Our science has grown to such proportions as to demand specialization. He who hopes to add anything to the sum of chemical knowledge must be content to seek the gems of discovery in a very small part of the whole field. A few years ago the family physician was doctor, surgeon, phlebotomist and dentist. Now he is a neurist, oculist, or orthopedist. If you want to be doctored all over you must call half a hundred specialists. So too with the chemist. Many of us can remember when physics and chemistry were so united as to be taught often by one man, who also employed his leisure moments in giving instruction in geometry and evidences of Christianity. Now a man devotes his whole life to the elucidation of a single phase of one of the many branches of chemical science. The necessity of this specialization is admitted by every one. The benefits which it brings we all enjoy; the dangers which it engenders we are too apt to forget. The one great danger is to the worker who goes deepest into the well after truth. He loses sight of the rest of the world. He is prone to think those who

are in the other wells are only diggers, and those who take the rough gems he finds and polishes them for use, mere sordid barterers. It thus happens that the one thing sought for is so magnified in the eyes of the worker as to make the value of all other things grow small. He who should above all have the largest views of the works of others thus often comes to have the smallest, and would if possible set up a chemical inquisition. There is no branch of our science which is to be crowned king and leader. Chemistry is a pure democracy, and all are equal therein. I have been more than once pained to see men of eminent achievements disclose the narrowness of their views by sneering at really good work not in their line. Gentlemen, this must not be! There is no eminence in science which makes a sneer becoming. My plea to-day in bidding you welcome to this convention is for a wider and deeper fraternity. The many sections of chemical science represented on our program are asked to join hands. For this reason the committee on program has desired that all members of the congress be given an opportunity to be present at the meetings of each section, and it is the earnest wish of those who have been charged with the preliminary work that we cultivate this community of feeling. Because, for instance, you may be investigating some problem in the domain where physics and chemistry touch, I beg of you not to despise the labors of him who in the domain of technical chemistry is striving to give a working body to your thought. Take him by the hand, listen to his speech, and it will do you good.

In this country our chemical workers have been widely scattered. Our friends from abroad must not, therefore, be surprised to find less *esprit du corps* among us than in their own countries. We have been whirled hither and thither in the wild molecular melange of a rapidly growing country. But now there are many centers of crystallization forming, and soon you will find among us more unity of action, more mutual helpfulness. One of the organizations which I have the good fortune to represent at this time is bringing into intimate relations large numbers of our American chemists and cementing them into a body which gives promise of lasting good in the future. Already

more than half a thousand American chemists have joined hands, and it is their united hand, big, brawny, and right honest in its grasp, which is extended to you to-day.

Thus in the lesson of this congress we learn not only of the special forms of activity as manifested in the titles of our papers, but we have before us a larger, unprinted program, a splendid plate, illuminated with the light of higher and broader views, bearing a greeting of good fellowship and fraternity and the promise of a more intimate union of all science.

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**PROCEEDINGS OF THE CONGRESS ON CHEMISTRY  
HELD IN CHICAGO, ILL., AUGUST 21  
TO AUGUST 26, 1893.**

MONDAY, AUGUST 21.

THE congress was opened by H. W. Wiley, chairman of the Joint Committee and president of the American Chemical Society, who gave an address of welcome to the foreign and American delegates, and suggested the establishment of a Triennial International Congress on Chemistry to meet at various centers.

It was voted to appoint a committee of five to take the recommendation under consideration.

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TUESDAY, AUGUST 22.

The session was opened by an address from Prof. E. Engler, of the Polytechnic School at Karlsruhe, who had been appointed honorary president for this day

The printed program of papers on analytical chemistry then followed as nearly as practicable, the following being presented in full or in abstract:

Opening Address. On Certain Distinct Advances in the Analytical Chemistry of Recent Years. Prof. A. B. Prescott, Ann Arbor, Mich.

On the Determination of Phosphoric Acid as Magnesium Pyrophosphate. Hugo Neubauer, Rostock.

Concerning the Method of Determining the Melting Point of Butter Fat. Prof. Adolf Mayer, Director of the Royal Experimental Station at Wageningen, Holland.

PROCEEDINGS.  
MINUTES OF THE COUNCIL OF THE AMERICAN  
CHEMICAL SOCIETY, 1893.

FEBRUARY 26, 1893.

The following is a copy of a communication received from H. W. Wiley, Washington, D. C. :

"We the undersigned respectfully petition the Board of Directors to incorporate the Washington Chemical Society as a local section of the American Chemical Society."

[SIGNED.]

H. W. Wiley,  
E. A. de Schweinitz,  
F. W. Clarke,  
Geo. Steiger,  
Charles E. Munroe,  
W. M. Mew,  
Robt. B. Warder.

Also a similar paper was received, signed by

Wm. H. Seaman,  
Jas. H. Griffin,  
Claude A. O. Rosell.

To the above application, the following was added :

"We the undersigned members of the council of the American Chemical Society, hereby request the Board of Directors to issue to the persons who have signed the above petition, a charter for the establishment of a local section of said society in the city of Washington, D. C."

[SIGNED.]

J. W. Mallet,  
A. B. Prescott,  
Alfred Springer,  
T. H. Norton,  
George F. Barker,  
Theodore G. Wormley,  
G. C. Caldwell,  
L. M. Norton,  
John Howard Appleton,  
C. F. Chandler,  
Albert C. Hale,<sup>1</sup>

<sup>1</sup> *Note.* As the constitution of the society does not provide for incorporating any other organization as a local section of the American Chemical Society, but merely for the formation of a local section "by the Board of Directors on receipt of a written request to that effect, signed by ten members of the society and endorsed by a majority of the council," the ten members above mentioned sent a new petition to the Board of Directors in conformity with the requirements of the constitution, and the Board of Directors thereupon issued to said ten members, under date May 10, 1893, a charter for the formation of a local section of the American Chemical Society in the city of Washington, D. C.

APRIL 12, 1893.

Prof. Edward Hart, Easton, Pa., was elected editor and third member of the Committee on Papers and Publications for the year 1893.

The following named persons were elected members of the society:

Cary, J. S., Chicago, Ill.  
Hoskins, Wm., Chicago, Ill.  
Heidenhain, H., Chicago, Ill.  
James, George, Chicago, Ill.  
Julian, Frank, South Chicago, Ill.  
Kennicott, C. L., Chicago, Ill.  
Liebmann, Adolph, Manchester, Eng.  
Low, W. H., Chicago, Ill.  
Puckner, W. A., Chicago, Ill.  
Sauer, H. E., Chicago, Ill.  
Stillwell, J. S., Prince's Bay, Staten Island, N. Y.  
Stuart, E. B., Chicago, Ill.  
Wickhorst, Max, Aurora, Ill.

APRIL 28, 1893.

The Committee on Papers and Publications, having received the following proposal, submitted it to the council, requesting them to approve or disapprove of making a contract with the Chemical Publishing Company in accordance with proposed terms. The council thereupon voted to approve a contract for an edition of seven hundred and fifty (750) copies at the rate of \$1.90 per volume in accordance with the terms of the proposal.<sup>1</sup>

## PROPOSAL.

Easton, Pa., April 17, 1893.

TO THE COMMITTEE ON PAPERS AND PUBLICATIONS, AMERICAN CHEMICAL SOCIETY.

Gentlemen:

We hereby propose to publish the Journal of the American Chemical Society, guaranteeing twelve (12) numbers per year, with a minimum of seven hundred and twenty (720) pages at the following rates:

For an edition of seven hundred and fifty (750) copies, at the rate of \$1.90 per volume; for an edition of one thousand (1000) copies, at the rate of \$1.80 per volume. This includes wrapping, mailing, and everything in the way of expense of publication, except cuts, which the Society shall pay for at cost. When requested by the author at the time the

<sup>1</sup> *Note.* At a meeting of the Board of Directors of the American Chemical Society held June 8, 1893, a contract for 1000 volumes of the Journal was authorized upon the terms of the proposition submitted by the Chemical Publishing Company.



manuscript is submitted, twenty reprints will be furnished without cost ; a larger number than this will be charged for.

It is understood that we are to have the use of one advertising page for our own advertising exclusively without cost to either party.

We guarantee that the paper and typography and illustrations shall be in every respect equal to those of the current volume of the Journal of Analytical and Applied Chemistry.

Respectfully,

CHEMICAL PUBLISHING COMPANY,  
per Eugene C. Foster, Manager.

The following named persons were elected members of the society :

Andrews, Geo. F., Cornell and Andrews, Providence, R. I.  
Hewitt, Edward R., 13 Lexington Ave., New York City.  
Westessan, J. P. L., Navy Yard, Washington, D. C.  
Williams, Henry J., 161 Summit St., Boston, Mass.

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MAY 1, 1893.

Ordered by the council that the report of the general secretary on the condition of the American Chemical Society be printed for the information of members and others interested.

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MAY 27, 1893.

Dr. C. B. Dudley, of Altoona, Pa., was elected a member of the council for the remainder of the year 1893, to fill the vacancy caused by the death of Prof. L. M. Norton, of Boston, Mass.

Prof. Norton's death occurred April 26, 1893.

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JUNE 7, 1893.

The following named persons were elected members of the society :

Adamson, George P., Easton, Pa.  
Baker, John T., Easton, Pa.  
Baker, Haydn M., M. D., 27 Hart St., Brooklyn, N. Y.  
Clymer, Lee S., Hellertown, Pa.  
Crawley, J. T., Audubon Park, New Orleans, La.  
Daly, B., 813 Fifth St., N. W., Washington, D. C.  
Foster, Eugene C., Easton, Pa.  
Green, Charles B., Easton, Pa.  
Jones, Clemens, Easton, Pa.  
Lee, Fitzhugh, Easton, Pa.  
Peckitt, Leonard, Catasauqua, Pa.  
Shimer, Prof. Porter W., Easton, Pa.  
Scholl, George S., Catasauqua, Pa.,  
Wiborg, F. B., Clifton, Cincinnati, O.  
Westenhoff, John Hermann, 17 W. 3rd St., Cincinnati, O.

The following was adopted :

" Resolved that the general meeting of the American Chemical Society for the summer of 1893 be held in Chicago at such date as may be determined by the committee appointed by the society to arrange with the World's Fair Auxiliary of the Columbian Exposition for an International Congress of Chemists."

Some days later the decision of the committee was announced as follows :

474 Waverly Ave., Brooklyn, N. Y.,  
June 27, 1893.

Prof. A. C. Hale,

Sec'y American Chemical Society ;

Dear Sir :

The committee appointed to co-operate with the World's Congress Auxiliary, to whom was referred the time at which the general meeting of the society for the summer 1893 shall be held in Chicago, have determined upon August 21 as the date for the beginning, and that it shall be held in conjunction with the World's Congress of Chemists beginning on the same date.

Very respectfully,

Wm. McMurtrie,

Chairman committee to co-operate with the World's Congress Auxiliary.

JUNE 15, 1893.

The following proposition of Prof. Edward Hart, of Easton, Pa., submitted to the Council May 15, 1893, and to the Board of Directors June 8, 1893, and agreed to by that body on the last mentioned date, was approved by the Council June 15, 1893 :

"(a) That I suspend the publication of my Journal with the June number, and for the rest of the year send to my subscribers the numbers of the Journal of the American Chemical Society instead; the expense of printing, binding, and mailing the additional copies required for this purpose to be defrayed by me. This plan gives my subscribers the society's journal for six months and will doubtless lead to a largely increased membership.

"(b) That in case the journal of the society shall at any time cease to be published by the Chemical Publishing Company, the American Chemical Society shall then, if I so desire, take all *complete volumes* of the Journal of Analytical Chemistry and of the Journal of Analytical and Applied Chemistry then in my hands, paying for them at the rate of one dollar (\$1) per volume, unbound. The total amount to be paid shall in no event exceed \$400. It is also understood that if additional copies of any number shall have been reprinted in the meantime, such additional copies shall not be included unless the society so desire."

- Recent Development of Mineral Tanning in the United States. Prof. S. P. Sadtler, Philadelphia, Pa.
- Petroleum in its Relations to Asphalt Pavements. Prof. S. F. Peckham, Ann Arbor, Mich.
- Natural Soda. Dr. T. M. Chatard, Washington, D. C.
- Chemical Industry of the United States. Henry Bower, Philadelphia.
- Condensation, Especially as Applied to the Distillation of Nitric Acid. Prof. Edward Hart, Easton, Pa.
- The Use of Electrolysis in Industrial Chemical Operations. Prof. J. W. Langley, Cleveland, Ohio.
- Petroleum. Prof. E. Engler, Carlsruhe.
- Asphalt; Its Occurrence, Composition, and Technology. F. P. Vandenberg, Buffalo, N. Y.
- Kryolith and its Industrial Application. Theodore Armstrong.
- The Fulminates; Their Preparation and Use. Prof. Charles E. Munroe, Washington, D. C.
- The Commercial Preparation of Calcium Phosphide. Prof. Charles E. Munroe, Washington, D. C.
- The Influence of Patent Laws on the Development of Chemistry. Prof. R. L. Biedermann, Berlin.
- The Manufacture of Essential Oils. Charles A. Serre.
- Some Chemical and Mechanical Considerations Involved in the Recovery of Animal Fibers. Louis J. Mátoš, Philadelphia.
- The Purification of Water. Prof. C. A. Doremus, New York.

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SATURDAY, AUGUST 26.

Prof. A. B. Prescott served as honorary president for the day.  
The following papers were presented:

DIDACTIC CHEMISTRY.

- Opening Address. Prof. W. E. Stone, Lafayette, Ind.
- Opening Paper. How Chemistry is Best Taught. Prof. C. F. Mabery, of the Case School of Applied Science, Cleveland, Ohio.
- The Education of Industrial Chemists. Dr. George Lunge, Zurich, Switzerland.
- The Teaching of Industrial Chemistry in Colleges. Henry Pemberton, Jr.
- Laboratory Work Must Be Subordinate and Auxiliary to the Presentation of Facts, Laws, and Theories by the Teacher. Prof. R. W. Jones, University of Mississippi.
- Quantitative Work for Beginners in Chemistry. Prof. W. A. Noyes, Rose Polytechnic Institute, Terre Haute, Ind.
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PHYSICAL CHEMISTRY.

Opening Address. The Cross-Fertilization of the Sciences. Prof. R. B. Warder, Washington, D. C.

On Chemical Energy. Prof. W. Ostwald, University of Leipzig.

The Energy Theory of Chemistry. (Comment upon Prof. Ostwald's Paper.) Prof. J. H. Trevor, Cornell University.

On the Atomic Weight of Oxygen. Prof. E. W. Morley, Cleveland, Ohio.

Apparatus for Promoting the Interaction of Liquids and Gases. Dr. Geo. Lunge, Zurich, Switzerland.

Stereochemistry of the Polymers of Acetic Aldehyde. Prof. W. R. Orndorff, Ithaca, N. Y.

SANITARY CHEMISTRY.

Efficiency of a System of Ventilation as Shown by the Amount of CO<sub>2</sub>. Ellen H. Richards, Boston, Mass.

The congress then adjourned, the chair voicing the general sentiment, that the efforts made had been followed with most gratifying success.

ROBT. B. WARDER, Secretary.

Persons in Attendance.

*Members of American Chemical Society.*

H. W. Wiley.	William Simon.	Wm. Frear.
Robert B. Warder.	E. H. S. Bailey.	Frank B. Dains.
K. P. McElroy.	Dr. Fred. Hoffman.	G. E. Barton.
W. D. Bigelow.	G. S. Fellows.	C. R. Stuntz.
G. de Chalmot.	Philip E. Chazal.	R. E. Blonin.
A. A. Bennett.	Pontus H. Conradson.	W. G. Brown.
J. H. Long.	Chas. L. Reese.	Wirt Tassin.
T. C. Trescot.	Albert L. Smith.	Geo. Steiger.
George A. Prochazka.	Morris Loeb.	Frank T. King.
Edward Hart.	J. Stockly Cary.	Chas. H. Miller.
W. A. Puckner.	Emil Furst.	A. H. Sabin.
Claude C. Hamilton.	Wm. Hoskins.	Jas. G. Hyndman.
E. H. Bartley.	Frank T. Shutt.	E. Sauer.
E. A. de Schweinitz.	Max H. Wickhorst.	Wm. McMurtrie.
W. W. Daniells.	Alfred Springer.	Thomas M. Chatard.
Wm. L. Dudley.	Henry Pemberton, Jr.	H. B. Nason.
August Eimer.	Charles L. Parsons.	Edward R. Hewitt.
J. N. Hurty.	Henry B. McDonnell.	W. O. Atwater.
William H. Krug.	Otis C. Johnson.	Frank Julian.
B. B. Ross.	W. A. Noyes.	R. W. Jones.
Albert E. Menke.	P. A. Mackay.	Alfred Hoffmann-Pinther.
Charles B. Dudley.	E. M. Danglade.	R. C. Kedzie.
A. S. Metz.	Thomas H. Norton.	A. B. Prescott.
F. W. Clarke.	S. P. Sharpless.	M. A. Scovell.
H. A. Huston.	Russell Elliott.	Wm. Bramwell.
Charles A. Doremus.	H. L. Grant.	J. F. McGregory.
Marcus Benjamin.	Herman Frasch.	J. T. McGill.
Ervin E. Ewell.	A. V. E. Young.	

*World's Congress.*

Richard H. Gaines.	W. A. Barrows, Jr.	E. Kennard Mitting.
M. H. Kauffman.	Julius Stieglitz.	Fred. A. Gritzner.
J. H. Kastle.	Rudolf de Roode.	W. H. Test.
Herbert W. Smith.	Henry E. Curtis.	Dr. George F. Payne.
G. L. Teller.	W. B. Rising.	J. E. Sinman.
Ludwig Saarbach.	T. F. Colin.	D. M. Henins.
B. W. Kilgore.	Mrs. Karl Thayer	Geo. H. Loesch.
Allen Hazen.	Pomeroy-McElroy.	W. A. Withers.
C. B. Cochran.	Chas. H. Herty.	J. E. Moore.
J. A. Heberly.	Alexander Smith.	Saml. Stockton Voorhees.
Vecheslav Tistshenko.	Henry Trimble.	L. L. Van Slyke.
Prof. A. Haller.	E. Goldsmith.	H. E. Smith.
C. W. McCurdy.	Dr. Otto L. Salomon.	A. L. Winton.
Russell W. Moore.	William Brady.	Robert Wahl.
Dr. E. J. Bughansen.	S. F. Peckham.	Arnold K. Reese.
Dr. Otto Mühlhaeuser.	Louis Ruhe.	H. P. Armsby.
Dr. Arthur W. Burwell.	Otto N. Witt.	Henry R. Chears.
J. B. Lindsay.	Dr. P. Naef.	William C. Stubbs.
C. Wellington.	H. N. Stokes.	James Boyce.
S. Tanaka.	E. Seeleholm.	E. A. Scribner.
V. O. Peterson.	R. O. Graham.	Jno. M. McCandless.
J. C. Foye.	B. S. Summer.	Louis Kahlenberg.
August Weingartner.	Fred. M. Wills.	B. D. Westenfelder.
R. P. Williams.	Sam. P. Sadtler.	C. O. Bates.
Arthur M. Comey.	B. von Herff.	S. M. Babcock.
W. E. Stone.	W. Gebhardt.	Mr. Goodell.
Dr. Rudolf Knietzsch.	Chas. Ford Langworthy.	H. Schweitzer.
Henry L. de Vilmorin.	H. Monmouth Armit.	E. E. Slosson.
C. F. Mabery.	George William Rolfe.	Wm. Louis Wilson.
Dr. G. Thoms.	H. L. Wheeler.	T. H. Clark.
John W. Langley.	Rich. J. Fischer.	Lyman F. Kebler.
Reuben Haines.	James C. Graves.	M. Gomborg.
Henry C. Wulf.	Henry R. Jessel.	Wm. H. Seaman.
H. W. Hillyer.		

CHEMICAL NOTES FROM THE COLUMBIAN EXPOSITION.  
II.

BY J. H. LONG.

Received August 14, 1893.

## DEPARTMENT H.—MANUFACTURES.

THE chemical exhibits of greatest interest are found in the Department of Manufactures. It must be confessed that as a whole the display is somewhat disappointing, because it is very unevenly distributed, one nation making more than one-half of the whole exhibit.

The nations showing chemicals are the United States, England, France, Germany, Russia, Sweden, and Italy. According to the catalogue, Switzerland makes one display of

chemicals, but it is not present, and what is shown by Italy and Sweden is of very slight importance. The chemical exhibits in this department can be best described under the heads of nationalities, beginning with the United States as in the official catalogue.

1. *The United States*.—While it is well known that the chemical industry of this country is not to be compared with that of several European countries, it is large and important enough to be better represented than is the case in the Columbian Exposition. While it is, perhaps, true that the best known firms are represented here, it is also true that others, turning out equally good products, are not here at all. The chemicals in the Manufactures building are found in Group 87, which contains thirty-eight entries. But it must not be supposed that all these have an interest for the general chemist. By some peculiarities in the method of classification we have, in this group, certain pharmaceutical products, soaps and perfumes, flavoring extracts and druggists' sundries, while similar products are found also in several other groups, some in the Department of Agriculture, and some in the Department of Liberal Arts. Of the thirty-eight American entries in Group 87 but thirteen need be listed here as likely to attract the attention of chemists in general. These are:

- J. J. Allen's Sons, Philadelphia, phosphorus and allied products.
- Henry Bower & Son, Philadelphia, general chemicals.
- Chesebrough Manufacturing Co., New York, petroleum products.
- Fritzsche Bros., New York and Leipzig, essential oils.
- Gordon Chemical Co., Cincinnati, glycerine.
- Hotchkiss Sons, Lyons, N. Y., essential oils.
- Marx & Rawolle, New York, glycerine.
- Pennsylvania Salt Manufacturing Co., Philadelphia, inorganic chemicals.
- Powers & Weightman, Philadelphia, general and pharmaceutical chemicals.
- Richard C. Remmey, Philadelphia, chemical stone-ware.
- Rosengarten & Sons, Philadelphia, general chemicals.
- Rössler & Hasslacher, New York, general chemicals.
- A. M. Todd, Kalamazoo, Mich., essential oils, menthol, etc.

What appears to be an oversight on the part of the exhibitors here is the absence of literature relating to the products manu-

ctured and the extent of the industries represented. The chemical public is interested, not only in the products themselves, but in the history of the exhibiting firms and the development of chemical industry in various countries. For business reasons American manufacturers appear to be slow in answering even the ordinary questions which were supposed to be asked during the collection of statistics for the last census. A competent authority from the United States Census Bureau explained to me recently that, "data connected with the statistics of chemical industry in the United States are among the most difficult to procure." It is certain that there is not enough material available in Chicago to enable one to write a satisfactory description of the industry as it exists in America to-day.

Several of the exhibits in the above list are very instructive, but we would all like to know more than is shown, and this without inquiring into what may be termed trade secrets, which the manufacturer has a right to withhold from the public.

2. *England*:—American chemists are well aware that Great Britain has a chemical industry of vast proportions, and would naturally expect to find a corresponding exhibition at the Columbian Exposition. But the facts do not satisfy the anticipation, as there are but nine exhibits of chemical interest and only four of these are striking or suggestive. The exhibits to which attention should be called are:

Lewis Berger & Sons, London, colors for printers and painters.

Brunner, Mond & Co., Norwich, alkalies, bleaching powder, etc.

Doulton & Co., London, chemical stone-ware.

United Alkali Co., Liverpool, alkalies, salts, etc.

Brunner, Mond and Company are the largest operators of the ammonia-soda process in Great Britain and their industry has grown from a small beginning to the present large proportions where about one-third of the total alkali made in England is made by the Solvay process. Their exhibit includes caustic and carbonated alkalies, silicates, and a number of other products of excellent appearance. It is unfortunate that the exhibit which is an interesting one, is not in the charge of a chemist capable of answering questions. Numerous visits to the collection have failed to find any one in charge.

The United Alkali Company is a combination of the leading manufacturers operating the Le Blanc and allied processes, and was formed in 1890 for "mutual protection" against ruinous competition among themselves and on the part of the ammonia-soda works.

This company claims to work, not as a trust, but as absolute owner of forty-five large chemical plants with railway lines, fleets of vessels, salt mines, stone quarries, etc. Their exhibit is attractive and will claim attention later for some details.

Manufacturers of chemicals on the large scale will be interested in the exhibit of stone-ware for factory work, made by Doulton and Company, of London. It includes various kinds of stone-ware employed in condensing or absorbing acid fumes, retorts, receivers, mixing pans, conducting pipes, acid cocks, acid pumps, and a great variety of small articles employed in chemical industry.

3. *France*.—The French exhibits arrived late and were greatly delayed in installation; at the present date no description of them appears in the official catalogue. There is, however, an official French catalogue on sale, which is badly arranged and is without a group index. According to this there are sixty-one exhibits of products which are classed under chemical and pharmaceutical industry, but some are either wanting or represented on a small scale, and others show perfumery, blacking, soaps, varnishes, etc., so that the number of chemical displays in the restricted sense amounts to seventeen. Those to which attention should be called are as follows :

Adrian et Cie., (Société Française de Produits Pharmaceutiques), Paris. General chemical products.

Buchet et Cie., (Pharmacie Centrale de France), Paris. General chemical and pharmaceutical products.

Hardy-Milori et Cie., Montreuil-sous-Bois. Organic and mineral pigments.

Société anonyme des matières colorantes et produits chimiques de Saint-Denis, (Poirrier), Paris. Organic coloring matters.

Société du traitement des quinquinas, Paris. Alkaloids.

Solvay et Cie. Varangé ville-Dombasle. Alkalies and salts.

Besides these there are several other exhibits of products from animal industry showing glues, gelatine, bone black, phosphorus,



etc., which are creditable. The several displays are arranged in a group of cases of similar design, forming a symmetrical whole.

4. *Germany*.—The representatives of German chemical industry began early to prepare an exhibit for the Columbian Exposition, and the results accomplished indicate that the matter was placed in good hands. The work of organizing an exhibit which should fitly represent the present condition of chemical industry in Germany was intrusted to a committee of nine prominent manufacturers, one from each of the eight sections of the German chemical trade union, and Dr. J. F. Holtz, of Berlin, as general chairman. To this committee eight other gentlemen were afterwards added and a study of the list shows that a selection of representative men was made. This committee concluded to make a collective exhibit and install it in a manner pleasing artistically as well as technically. The advice of an architect was sought and as a result the cases containing the collective exhibit were made, brought over and put up around a central pavilion, serving as an office, according to a design which is symmetrical and satisfactory from every standpoint. Seventy-one firms finally united in making the display, which was placed in charge of Mr. Richard Fischer, of Berlin, who represents the interests of all the exhibitors in a very fair and impartial manner, and at the same time does all in his power to assist the chemical public to an understanding of everything in his charge.

Very peculiar conditions exist to-day in the chemical industry of Germany which make such an exhibit possible. The manufacturers are united in a society which is termed the "Verein zur Wahrung der Interessen der chemischen Industrie Deutschlands" (society for the protection of the interests of German chemical industry) and which holds general meetings once a year. The organ of this society is the well known journal, *Die chemische Industrie*, edited by Dr. Emil Jacobsen, in Berlin, and this handles all questions of practical interest to the several industries united in the organization.

German chemical manufacturers are further united in a trade union (Berufs-Genossenschaft) which is rendered necessary by

the laws governing accident insurance to German workmen. This great union is, for convenience, grouped in eight sections geographically located as follows: (1) Berlin; (2) Breslau; (3) Hamburg; (4) Cologne; (5) Leipzig; (6) Mannheim; (7) Frankfurt a. M.; (8) Nuremberg. Chemical manufacturers are, therefore, so organized that co-operation in a display such as is made in Chicago is a thing easily secured, and the value of co-operation, for this purpose at any rate, is abundantly demonstrated by the success achieved in the installation of the collective exhibit.

Seven great branches of chemical industry are represented in Chicago and they may be divided as follows:

(a) Fundamental industries. Here we have the manufacture of strong acids, alkalies, and common chemicals in general employed by the soap maker, in the paper industry, in the glass industry, and elsewhere on the large scale.

(b) Pure chemical preparations for special purposes. Under this head appear the chemicals used in photography, in pharmacy, in laboratories as reagents or for purposes of investigation. The chemicals of this class are best known to American chemists, coming from the great houses of Schuchardt, Merck, Kahlbaum, Trommsdorff, De Haen, and others.

(c) Coal tar products, particularly the artificial coloring matters.

(d) Inorganic and organic pigments for the use of lithographers, printers, painters, porcelain glazers, etc.

These four groups belong to chemical industry proper. Then we have:

(e) Animal products, including especially glue, and gelatine for household and photographic uses.

(f) Fats, oils, soaps, and cosmetics.

(g) Chemical apparatus and accessories.

To show the extent of the exhibit a full list of the firms exhibiting in groups (a), (b), (c), (d), and (g) is here given.

Aktiengesellschaft für chemische Industrie, Mannheim, acids, alkalies, salts, etc.

Aktiengesellschaft für chemische Industrie, Schalke in Westphalia, acids, alkalies, general chemicals.

Arsenic-Berg-und Hüttenwerk, "Reicher Trost," Reichenstein in Silesia, arsenic ores and preparations.

Bernhardi, J., Leipzig, pharmaceutical preparations.

Chemische Fabrik auf Aktien (vormals E. Schering, Berlin), pharmaceutical chemicals.

Chemische Fabrik Bettenhausen, Marquart & Schulz, Bettenhausen near Cassel, technical and pharmaceutical chemicals.

Chemische Fabrik Griessheim, Frankfurt, general chemicals.

Chemische Fabrik, vormals Hofmann & Schötensack, Ludwigshafen, general chemicals.

Chemische Fabrik Kalk, Cologne, Stassfurt salts, saltpeter, etc.

Chinin Fabrik Braunschweig, Braunschweig, alkaloids, especially cinchonas.

Farbenfabriken, vormals Friedrich Bayer & Co., Elberfeld, pharmaceutical chemicals.

Goldschmidt, Th., Essen, tin and zinc salts, mordants.

Dr. Graf & Co., Berlin, metallic paints, etc.

Harrmann & Reimer, Holzminden, organic chemicals.

E. de Haen, List vor Hannover, general chemicals.

Dr. F. von Heyden's Nachfolger, Radebeul, organic pharmaceutical chemicals.

Knoll & Co., Ludwigshafen, organic pharmaceutical chemicals.

Köpp & Co., Oestrich, Rheingau, general chemicals.

E. Merck, Darmstadt, general chemicals; also a large exhibit in special building.

Rhodium, Gustav, Burgbrohl, inorganic chemicals.

Riedel, J. D., Berlin, pharmaceutical chemicals.

Dr. Schaeffer, Charlottenburg, anhydrous ammonia and salts.

Dr. Schuchardt (Inhaber, Dr. Albert Weil), Görlitz, general chemical preparations.

Stassfurter Chemische Fabrik, Stassfurt, Stassfurt salts, cyanides, etc.

H. Thiemann, Jr., Stolp, general chemicals, amber.

Verein Chemischer Fabriken, Mannheim, general chemicals.

Vereinigte Fabriken, Zimmer & Co., Frankfurt and Feuerbach, alkaloid preparations.

Wasmuth & Co., Ottensen, pharmaceutical preparations.

Wassmuth & Co., Barmen, antiseptic preparations.

Dr. Witte, Rostock, pharmaceutical chemicals.

Gödecke & Co., Leipzig, essential oils and ethers.

Heine & Co., Leipzig, essential oils and artificial products.

Em. Kern, Edenkoben, cognac oils and tartars.

Kölling & Schmitt, Zerbst, essential oils and essences.

Brüder Richter, Leipzig, essential oils, menthol, etc.

G. Bormann Nachfolger, Berlin, pigments for various purposes.

Gademann & Co., Schweinfurt, a. M., mineral pigments.

Dr. Emil Jacobsen, Berlin, colors for artists and other purposes.  
Kast & Ehinger, Stuttgart, printing and lithographing colors.  
Bruno Lampel, Cologne-Ehrenfeld, mineral pigments.  
Michel & Morell, Eppstein and Höchst, black pigments.  
Moritz & Co., Hangenbieten, copying inks.  
Johann Gottlieb Müller & Co., Stuttgart, colors for artists.  
W. Rannefeld & Co., Blankenburg, mineral pigments.  
Dr. Eugen Schall, Stuttgart-Feuerbach, lacquers for metals, etc.  
G. Siegle & Co., Stuttgart, colors for printers and lithographers and for other purposes.  
Vereinigte Ultramarinfabriken, Nuremberg, ultramarine.  
Aktien Gesellschaft für Anilinfabrikation, Berlin, colors and colored samples.  
Badische Anilin und Sodafabrik, Ludwigshafen, general chemicals and coloring matters.  
Chemische Fabriken, vormalig J. W. Weiler & Co., Cologne-Ehrenfeld, coal-tar products.  
Rudolf Rütgers, Berlin, crude and purified coal tar products.  
William Pearson & Co., Hamburg, antiseptic preparations.  
Deutsch-Oesterreichische Mannesmannröhren Werke, Berlin, steel flasks for condensed gases.  
W. C. Heraeus, Hanau, platinum ware for laboratory and industry.  
Königlich Preussische Porzellan Manufaktur, Berlin, porcelain ware for laboratory and industry.  
Tritschler, Winterhalder & Co., Voithenberghütte, laboratory apparatus of glass.

It will be observed that many of these firms are already well known in the United States, while others are making, perhaps, their first request for American recognition. As a whole, the collective display must be described as a success of the first magnitude, and deserving of the most careful study on the part of American chemists visiting Chicago.

I will make no attempt here to describe it in detail, but will leave that part of the discussion for a subsequent paper. I will only add that Mr. Fischer is supplied with literature which will answer almost every question which one may wish to ask about the chemical industry of Germany, and from which many of the points given above are derived.

5. *Russia*.—The extent of chemical industry in Russia is probably but little understood in the United States because of absence of trade and general lack of acquaintance with the language; however, five exhibits are shown in the Russian section which

indicate a fair condition of chemical activity. These are as follows:

Brömme Brothers, St. Petersburg, organic chemicals.  
Technological Institute, St. Petersburg, general chemicals.  
Köhler & Co., Moscow, general chemicals.  
Oushkoff & Co., Moscow, general chemicals.  
Tentelawa Chemical Factory, St. Petersburg, general chemicals.

No literature is at hand showing the extent of the industries here represented.

(6) *Sweden* makes no exhibit of chemicals proper. The products of an acetic acid factory are shown and the Munktell filter paper is displayed by Sargent and Company, of Chicago, in the Swedish building.

(7) *Other Countries*.—Scattered through the various buildings are displays which in a certain sense have an interest for chemists. But practically everything belonging to chemical industry proper has been referred to in the above. It must also be mentioned that the official catalogues contain a great many mistakes, besides being silent as to displays from France, Russia, Spain, and other countries. It is in many cases difficult to find exhibits looked for.

*Other Exhibits*.—In the Manufactures building the German universities have united in showing a valuable collection of books, photographs, instruments, and preparations, all of the highest scientific interest and importance. Many pieces of apparatus shown are famous in the history of science, as with them original or fundamental determinations have been made.

Several of our leading American schools, notably Harvard, the Massachusetts Institute of Technology, the University of Pennsylvania, Johns Hopkins, Princeton, and Yale, have made displays highly interesting and valuable as showing the advance of scientific education in the United States.

In the Electricity building, besides the displays of electrical instruments and machinery of all kinds, there are two exhibits to which attention must be directed, as otherwise they may be overlooked because of their unfortunate location in the gallery. One is a collective display of physical and chemical apparatus

made by many of the leading German factories. Very interesting exhibits are made by the following:

Schmidt & Haensch, Berlin.

A. Krüss, Hamburg.

Karl Zeiss, Jena.

Steeg & Reuter, Hamburg.

Staudinger's successor, Giessen.

Bunge's successor, Hamburg.

Grossherzoglich saechsische Pruefungsanstalt für Glas Instrumente, Ilmenau.

The other important exhibit here is made by the Physikalisch-Technische Reichsanstalt, Charlottenburg, near Berlin, and consists of normal and standard instruments for various purposes, samples of material, diagrams, publications, etc., which are interesting to anyone acquainted with the work of the institution.

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## THE DEVELOPMENT AND EXTENT OF THE FERTILIZER INDUSTRY.<sup>1</sup>

BY CHARLES U. SHEPARD, M. D., CHARLESTON, S. C.

THE fertilizer industry pre-eminently owes its origin to the scientific recognition of the indispensability of phosphoric acid as an element of plant food; its steady growth has reflected the agricultural appreciation of its use, while the stupendous strides in this branch of trade have especially followed the development of new phosphatic deposits, whose yield has furnished the basis of most artificial manures.

As powerful coadjutors in building up the fertilizer industry to its present dimensions, may be mentioned the development of the Stassfurt potash mines and the South American nitrate of soda beds, the utilization of pyrites (chiefly from Spain and Portugal), the Thomas slag from the steel works, ammonium sulphate, cotton-seed and other meals, and the valuable side products from the enormous slaughter houses of the present day. All of these agencies have contributed largely to the modern growth of the fertilizer industry; nevertheless a brief study of the history of the manufacture and trade in commercial manures

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will show that its inception and expansion are chiefly due to the demand for and supply of phosphoric acid for agricultural purposes.

Bone and ivory clippings from the knife and button factories of Sheffield, England, were probably the first purely phosphatic manures. This material, amounting to about 1000 tons annually, was regarded as waste until the middle of the last century. Neighboring farmers began to use it on their lands, and so convincing were the results of its application, they soon became willing to meet the constantly advancing price of an article which, originally, was considered barely worth the trouble of hauling to their fields. The same experience was had at a similar factory near Puy-de-Dome, France, although the good results from the utilization of bone-waste do not appear to have been as thoroughly appreciated as in England. In 1774, Hunter first openly advocated the agricultural use of bones. The first experiments with bone meal, on beets, were made in 1775, in Lincolnshire.<sup>1</sup>

From such feeble beginnings, and so comparatively recently dated the consumption of phosphatic manures; they failed, however, to assume any great commercial or agricultural importance until after 1820.

Very naturally the effect of bones on crops received an erroneous interpretation in the days when agricultural chemistry was hardly dreamed of. Thus, Albrecht Thaer, the great agricultural writer, at the close of the last century and in his introduction to the study of English agriculture, observed, "Burnt bones have the effect of lime." And again in 1833, in his *Principles of Rational Agriculture*, he attributed to the gelatine contained in bones, the good results from their use. About the same time John Nepomuk von Schwerz wrote in his *Introduction to Practical Agriculture*: "The effect of bone-meal is not inconsiderable, even after the extraction of the fatty matter." Fawtier in writing of the value of the several components of bones, observed: "We can neglect one of the earthy components, *viz.*, phosphate of lime, because it is indestructible and insoluble. It cannot

<sup>1</sup> "Die Natürlichen Phosphate," by Dr. L. Meyn, and "Chimie Agricole," by Prof. P. P. Dehérain, have afforded me many of these historical data.

serve as manure." If later the beneficial action of bones was acknowledged, it was almost wholly attributed to their gelatin by such writers as Payen.

But another and the true significance of bone manure soon obtained foothold. The presence of phosphorus in seeds had been discovered by Polt, and afterwards verified by Margraff, Vauquelin and Th. de Saussure: Basing his opinions on their researches, Justus von Liebig attributed the agricultural effect of bones to their content of phosphate of lime. The Duke of Richmond's direct field experiments on the use of bones were instituted in 1843. They apparently demonstrated that the action of calcined or boiled bones (*i. e.*, deprived in whole or in part of their grease and gelatin) is not inferior to that of crude and fresh bones. His conclusion, which controverted the prevailing opinion, was that the fertilizing principle of bones lies neither in grease nor in gelatin, but rather in phosphate of lime, and more particularly in phosphoric acid and not lime.

Meanwhile the agricultural application of and consequent demand for bones outran the scientific investigations as to their mode of action. Factories for grinding bones were established in England, France, and Germany. The cultivation of the sugar beet and the manufacture of sugar on the Continent enormously increased the demand for bones. They were no longer regarded as refuse; but, on the contrary, they were everywhere carefully collected and shipped to great commercial centers or locally applied to the crops. In 1859, Great Britain imported 84,000 tons; in 1872, 97,778 tons, worth £642,715. But a substitute was at hand, which should relieve the farmer in his competition with the sugar refiner. Coprolites had been discovered in France and England, and their composition ascertained. These discoveries remained inoperative until after the experimental investigations of the Duke of Richmond, before alluded to, and those of Justus von Liebig with superphosphates.

Liebig recommended in 1840, the employment of sulphuric acid to dissolve osseous phosphate of lime, and, thus to render it more subservient to the wants of vegetation. Shortly thereafter, John Bennett Lawes, the great English manufacturer of chemical manures and yet more distinguished experimenter in



agricultural chemistry, erected a factory for the treatment of coprolites and similar phosphates according to Liebig's plan for utilizing bones.

Immediately the interest in phosphatic material of every kind was stimulated by the promulgation of their value. The search for phosphatic deposits extended to all accessible parts of the world. A vast number and variety of phosphates were discovered and developed. Nevertheless it was not until the South Carolina beds had been opened to commerce and manufacture, that the treatment and manipulation of mineral phosphates, which thus far has constituted the main function of the fertilizer industry, began to assume the rapid expansion which has latterly characterized it.

The inauguration of the South Carolina phosphate industry occurred in the winter of 1867-68.

At a time when the prostration following an exhausting war and a social revolution had depressed all the former commercial and agricultural industries of the Carolina seaboard, and men were casting about for the means to rehabilitate their broken fortunes; when the deposits of Peruvian guano and West Indian phosphates had begun to exhibit signs of their ultimate, perhaps speedy, exhaustion, and remaining sources were proving entirely inadequate to supply the rapidly increasing demand for mineral phosphate of lime, which had been shown to be susceptible of conversion into a substitute for the phosphates contained in guano and bone; then, and as a generally appreciated relief, began the practical utilization of the Carolina phosphate beds.

The necessity of the restitution to enfeebled lands of the mineral constituents of plant food, so ably presented by Justus von Liebig, had duly impressed the minds of all enlightened farmers, particularly those in the older countries. The settlement of the vast plains of the American northwest and the active shipment from its virgin soil of cereals and animal products at prices which defied competition by the old system of agrarian operations, necessitated intensive agriculture. A stricter study into every detail of cost on the farm and the practice of rigid economy throughout had well nigh dethroned bulky

domestic manures from their long vaunted supremacy. The use of quickly-acting fertilizers for shortening the period of plant growth, and especially to permit of the successful raising of money-crops beyond their natural thermal belts, had become established.

Simultaneously with the development of the Carolina deposits, occurred that of the Stassfurt potash salts, and shortly thereafter that of the nitrate of soda beds on the Pacific coast of South America. Meanwhile the substitution of sulphur from pyrites—often obtained as a side product—for the more expensive Sicilian brimstone, and the introduction of great improvements in the methods of manufacturing chemical manures, combined to cheapen the cost of their production. With a ready supply of the other mineral constituents of plant food, a greater demand has naturally followed for what has been long regarded as the very foundation of artificial fertilizers, *viz.*, phosphate of lime.

Thus were afforded, and at a time of their greatest need, to the people of the Carolina seaboard, the manifold blessings which flow from a great and comparatively remunerative industry; and to farmers at large commercial manures of better quality and at cheaper cost than they had before enjoyed. Possessing about the same content of phosphoric acid as the best coprolites and the various bone articles which had previously served for the manufacture of superphosphates, and mixing very kindly with sulphuric acid, the South Carolina phosphates were gladly utilized by all the trade in artificial fertilizers, except by those engaged in making the high grade goods sold in Germany. The growth of the South Carolina industry has been fairly steady, as the yearly production of the mines prove:

	Tons.
1868, year ending May 31 .....	12,262
1871, " " " " .....	74,188
1874, " " " " .....	109,340
1878, " " " " .....	210,322
1885, " " " " .....	395,403
1889, " " Dec. " .....	541,645
1891, " " Aug. " .....	572,949
1892, " " " " .....	548,396

According to Maj. E. Willis the production of South Carolina phosphates for the years 1891-2 and 1892-3, ending August 31, was as follows :

	From Charleston, 1891-92, tons.	From Beaufort, 1891-92, tons.	From Charleston, 1892-93, tons.	From Beaufort, 1892-93, tons.
Foreign shipments...	4,396	120,058	175	177,893
Coastwise " ...	143,627	30,602	121,939	96,720
Interior .....	58,713	10,000	39,342	12,500
Consumed .....	165,000	16,000	155,000	15,000
	<hr/> 371,736	<hr/> 176,660	<hr/> 316,456	<hr/> 302,113
Grand total.....	1,166,965			

The shipments from the State's territory, almost wholly confined to the Beaufort district, were for the same year (ending August 31, 1892), 156,095 tons; they promise to approximate 250,000 tons for the present year.

THE AMOUNT OF PHOSPHATE ROCK MINED AND REMOVED FROM THE RIVERS OF SOUTH CAROLINA, BEING THE PROPERTY OF THE STATE, FROM SEPTEMBER 1, 1892, TO SEPTEMBER 1, 1893, ACCORDING TO STATE INSPECTOR JONES, "THE NEWS AND COURIER," SEPTEMBER 19, 1893.

	Tons on hand first of year, estimated.	Tons mined during year, estimated.	Tons removed during year.	Tons on hand last day of year, estimated.
Coosaw Co .....	40,370.00	98,631.00	110,719.99	15,411.00
Carolina Mining Co....	11,631.00	56,500.00	63,521.60	6,826.00
Farmers' Mining Co...	15,675.00	36,576.00	46,093.95	4,000.00
Beaufort Phosphate Co.	11,048.00	21,184.00	27,613.96	4,927.00
Ashley Phosphate Co..	.....	169.67	169.67	.....
J. C. Nelson .....	305.75	579.25	487.00	407.00
James O'Hear .....	455.25	177.74	.....	623.00
James Reed.....	60.00	487.00	630.00	.....
F. W. Wagener & Co..	12.00	122.54	122.54	.....
Total.....	79,557.00*	214,427.20*	249,358.71	32,194.00

\*Corrected.

The Florida phosphate beds have recently attracted great attention not only from capitalists seeking suitable investments, but also from all phosphate miners and those engaged in the fertilizer trade.

In view of the many publications on this subject which have latterly appeared and because I do not feel at liberty to digress

from the topic which I have chosen, I will content myself with simply quoting the production for the past few years of Florida phosphates of all varieties, *viz.* :

	Tons.
1888 .....	3,000
1889 .....	4,100
1890 .....	46,501
1891 .....	112,482
1892.....(about)	290,000

The shipments for 1892 consisted of about two-thirds "hard rock" and one-third "pebble" phosphates. They comprised 283,221 tons, of which 225,090 tons were exported to foreign ports. (Letter of Mr. E. W. Bailey, of Fernandina.) The local consumption of phosphates in Florida is estimated at a few thousand tons.

FLORIDA HARD ROCK AND PEBBLE PHOSPHATE, 1892 (E. WILLIS).

	—Hard rock—		—Pebble rock—		
	Domestic.	Foreign.	Domestic.	Foreign.	
Punta Gorda ..	.....	.....	21,809	44,314	
Fernandina ...	5,520	119,492	.....	.....	
Tampa .....	1,000	45,590	20,816	2,808	
Savannah .....	.....	7,412	.....	.....	
Brunswick ....	.....	18,061	.....	.....	
Jacksonville ..	.....	.....	.....	.....	
Rail .....	4,000	.....	19,300	.....	
Consumed.....	1,000	.....	3,000	.....	
	<u>11,520</u>	<u>190,555</u>	<u>64,925</u>	<u>47,122</u>	
		202,075		112,047	
Total tons...					<u>314,122</u>

I have hesitated about discussing before so intelligent and professional an audience the necessity of the fertilizer industry. But there may be some present who, while admitting the general proposition that a restitution of the elements of plant food should accompany the steady depletion which continued cropping entails, have not considered the extent of this drain—that enormous waste which even now the utmost energies of the trade in commercial manures cannot compensate for. Centuries of harvesting in the ancient grain producing countries of the world have reduced the original stock of assimilable phosphoric acid to a point where the cereals may no longer be profitably culti-

vated. A natural recuperation, if possible, involves cycles of time. Nations recover from the effects of disastrous and sanguinary warfare; but no human endurance can withstand widespread sterility in a land. The population must seek other and more fertile regions, or be doomed to abject poverty or slow extinction. Man is essentially a squanderer of phosphoric acid. To his agency, pre-eminently, may be ascribed its exhaustion in the soil. The greater part of this precious ingredient which enters so largely into his own frame and the composition of his food, as also of the animals subservient to him, is allowed to flow into the sea; where at the greatest depths of ocean-dredging it has been discovered, apparently now building new phosphatic deposits, some nodular and others as a replacement of old animal forms.

Dehérain has valued the phosphoric acid annually contained in the solid and fluid dejections of the French population (thirty-six million souls) at nearly \$4,000,000. Johnson has calculated that the liquid manures carried off each day by the sewers of London would fertilize near 60,000 acres of sterile land, and thus might support 125,000 individuals for one year.

Delagarde has calculated the annual waste of plant food in rural France at the enormous sum of \$400,000,000, that being the commercial value of the material adequate to replace the dissipated ingredients.

China offers an example to the world in the care with which all animal remains and manures are restored to the soil. It is unquestionably due to this economy that its territory can support two human beings to the acre. In some of its provinces the ratio is greater, as in Pekin and Tchenkon, where one acre subsists six to eight.

If fecal matter were saved in France to the extent of only twenty per cent. more than is now the case, it should not be compelled to import in some years ten million dollars worth of grain; it might, on the contrary, export nearly twenty millions worth per annum (Bobierre). The use of domestic manure extends back to the earliest times in much the same manner and to the same effect as at present; and yet it has not prevented the exhaustion of many fertile lands nor averted the gradual

decline in productiveness of European and other lands now cultivated for a long period.

The report of the international jury at the Universal Exposition of 1889 by M. Grandeau, shows the amount of the most important constituents of plant food annually abstracted from French soils, and their value. The yearly depletion is of

	Tons (metrical).	Value per ton.	Total value.
Nitrogen .....	600,000	at 1600 francs	960,000,000 francs
Phosphoric acid....	300,000	" 300 "	90,000,000 "
Potash.....	775,000	" 450 "	348,000,000 "
		(\$279,600,000)	1,398,000,000 "

The production of farm manure for 1892 was estimated at 84,000,000 tons, containing of

	Tons.
Nitrogen .....	327,600
Phosphoric acid .....	151,200
Potash .....	378,000

Without allowing for any waste in the stable and other manure of the farm, the deficit for the year should stand :

	Tons.	Per cent.	
Nitrogen.....	272,400	or 45.4	} Per cent. of the yearly depletion.
Phosphoric acid.....	148,800	" 49.6	
Potash.....	397,000	" 51.2	

To restore this deficit would be required of the following chemical manures:

	Tons.		Tons.
Nitrate of soda.....	1,747,000	Superphosphate .....	1,240,000
Sulphate of ammonia ...	1,463,000	Potassium chloride .....	1,985,000
Tribasic phosphate.....	876,000	Kainite.....	3,300,000

Robert Hasenclever has calculated that the yearly crops abstract from the soil of Germany 640,276 tons of phosphoric acid; that the entire animal excreta together with the litter contain 553,572 tons of phosphoric acid, but that fully one-half of it is lost to agricultural use, which would leave an annual deficit of 363,490 tons. Against these figures are to be put 156,020 tons phosphoric acid contained in the yearly application of chemical manures; the result is an annual abstraction of over 200,000 tons phosphoric acid from German fields.

In view of modern experience and for the needs of a general agriculture, there appears to be more necessity of replacing phosphoric acid than either nitrogen, which by natural agencies may be restored from the atmosphere, if slowly (Dehérain), or potash, of which there is usually a practically greater supply in the soil and which may be replaced by soda, at least to a slight extent under favorable conditions.

As to the requisite amount of restitution, Drechsler arrived at the following conclusions:

"1. All cultivated plants require for their best development a greater supply of assimilable nutritive principles in the soil than what they abstract during the period of growth. Their yield is proportionate to the amount of the ingredient which offers to the plant the smallest quantity in an assimilable condition.

"2. If a soil contains less plant food than is requisite for the production of the crop, it can reproduce an equal harvest of the same kind only when the ingredients abstracted from it are restored.

"3. It is necessary to restore in quantities sufficient to re-establish the productiveness of lands, the ingredients abstracted in the produce which the soil does not contain in excess or are not in a proper state of division (for assimilation).

"4. At each manuring it is necessary to so augment the fund of assimilable food in the soil that the available amount of each ingredient shall be sufficient for the production of normal agricultural crops until the occurrence of the next fertilization."

That without abundant restitution, it is simply a question of time until all soils must become practically exhausted, our own short American experience amply teaches. A century ago the farmers about Albany and New York, produced thirty to forty bushels of wheat, where their successors now obtain only ten or twelve. A recent correspondence with agricultural authorities throughout the now central states and those lying to the west of them, has clearly demonstrated how comparatively soon the necessity for using commercial manures occurs even in our briefly occupied and originally fertile central territory. A western state will indignantly reply to a question as to the condition of the commercial manure-trade within its borders, with the

statement that so great is its fertility that absolutely no restitution to its fields is required. Its neighbor to the east admits the use of stable manure, as a supplement to the original fertility, at least for some crops. Yet to the eastward, and there come vague reports of artificial manures being used, if only in small quantities. But as soon as the north and south line is reached which divides our population into the eastern and western halves, statistics of consumption become attainable, and their testimony proves an ever increasing trade in these commodities.

The fertilizer industry stands no longer on the defensive; except in ignorant communities, its tone is no longer apologetic. Its mission is noble, if simple, *viz.*, to make two ears of corn where now there is only one and soon there may be none. Its functions are to provide an adequate supply of food for man, animal and plant; to enable the farmer to carry out the old saying, "Feed your land and it will feed you." Its importance must be weighed not only by its actual achievements, but by the effects of its absence. A signal proof of its necessity, lies in its stupendous development during the past twenty-five years. No statesman can afford to underrate its influence or antagonize its activity, since they serve to invigorate agriculture, whether for the direct support of animal life or for the production of money crops, thus enhancing the value of lands which otherwise might soon be worthless.

#### THE SOURCES OF THE CHIEF INGREDIENTS OF COMMERCIAL FERTILIZERS.

*Peruvian Guano.*—The dimensions of the trade in Peruvian and similar guanos in times past have an additional value for us as they reveal the void which its present shriveled size has left, and they indicate the necessity for providing a substitute at least in quantity. A real equivalent has never been found; nor is it probable that so efficacious and abundant a combination of plant food will be discovered in the future.

The extent of the trade in these natural bird guanos was enormous so long as the supply was unimpaired, but one by one the deposits yielded to the eager demand for the precious and costly material. The quantity of guano exported from Peru from February 19, 1842, to December 21, 1867, amounted to



7,175,194 tons, valued at \$218,693,625; and in 1871 and 1872, to 1,181,327 tons, valued at \$44,915,451. The United States imported in the period 1848 to 1858 707,408 tons.

By no means all bird guano came from Peru, as the following table of the shipments to Europe during the years 1841 to 1857 will show:

	Tons.
From Peru .....	1,664,662
“ west coast of Africa.....	305,807
“ South Africa.....	76,042
“ Chili .....	106,602
“ Patagonia .....	73,485
“ Bolivia .....	24,667
“ other localities .....	122,383
	<hr/> 2,373,648

Great Britain received in the period 1884 to 1888, 188,421 tons of bird guano, worth £1,596,020, and exported 41,840 tons, valued at £343,562. The present exportation of Peruvian guano does not probably exceed 50,000<sup>1</sup> tons annually, of which one-half goes to the United Kingdom. After manipulation it is largely shipped to the colonies.

*Nitrate of Soda.*—The nitrate of soda trade from the Pacific coast of South America has assumed gigantic proportions ever since the shipments of Peruvian guano began to wane, as may be seen from the following table which exhibits the exportation and consumption during the past few years.

	Exportation from South America, tons.	Consumption— in		Total consumption, tons.
		Europe, tons.	in America, tons.	
1888.....	754,000	637,000	68,000	705,000
1889.....	930,000	655,000	79,000	734,000
1890.....	1,035,000	780,000	104,000	884,000
1891.....	753,000	830,000	98,000	928,000
1892.....	795,000	785,000	97,000	882,000

These figures also show the preponderance of the supply over the demand, which caused a fall in price and later brought about an agreement among the producers to reduce the shipments to 800,000 tons in 1891 and 900,000 tons in 1892.

<sup>1</sup> Voss and others reckon it higher, even to 100,000 tons.

The present (1892) consumption of nitrate of soda by countries is approximately as follows:

	Tons.
Germany .....	330,000
France .....	200,000
Great Britain .....	110,000
Belgium .....	100,000
Holland .....	40,000
Spain and Italy .....	10,000
United States .....	100,000
	<hr/> 890,000

By no means all of this vast supply is directly employed by agriculture, very considerable parts being used in the manufacture of gunpowder, sulphuric acid, and chemicals. Nevertheless, the greater portion of the importation finds agricultural use in Germany and other countries.

*Sulphate of Ammonia.*—This began to find considerable employment in agriculture in the sixties. Its present production in Europe has been given as follows:

	Tons.
England .....	143,000
France .....	25,000
Belgium .....	10,000
Germany .....	30,000
Other countries .....	10,000
	<hr/> 218,000

According to another authority, Bradbury & Hirsch, of Liverpool, the production in and exportation from Great Britain for 1892 was:

	Tons.
Exportation to Germany, Denmark, Sweden, and Russia....	33,000
“ “ France, Spain, and Italy .....	36,000
“ “ Belgium and Holland .....	24,000
“ “ America and colonies .....	18,000
Consumed in Great Britain .....	43,500
Stock on hand .....	3,500
	<hr/> 157,000

1892 total production in Great Britain..... 157,000  
*Stassfurt Potash Salts.*—The total production of the syndicate of Stassfurt miners for 1891 was as follows:

	Gross Tons.
Chloride of potassium.....	134,162
Sulphate of potash.....	17,980
Double sulphate of potash and magnesia, calcined.....	11,398
“ “ “ “ “ “ crystallized .....	1,052
Manure salts, calcined.....	3,076
Kieserite .....	28,559
Kainite and sylvinite.....	413,507
Carnallite .....	39,441

The industrial and agricultural use of the chloride of potassium, eighty per cent., and sulphate of potash, ninety per cent., is as follows:

	—Industrial—		—Agricultural—	
	Germany, tons.	Foreign, tons.	Germany, tons.	Foreign, tons.
Chloride .....	42,498	38,115	1,300	49,430
Sulphate .....	4,648	4,500	110	8,722

According to Hasenclever the following quantities of kainite were used in Germany in the years mentioned:

	Tons.
1880.....	23,763
1885.....	55,320
1888.....	105,231
1889.....	150,341
1890.....	178,031

The consumption of Stassfurt potash salts for the year 1891 was as follows:

Countries.	80 per cent. chloride of potassium, gross tons.	90 per cent. sulphate of potash, gross tons.	Kainite and sylvinite, gross tons.
Germany .....	43,798	4,758	240,000
Austria .....	2,550	60	....
England .....	12,310	1,650	....
Scotland .....	8,150	1,385	....
France.....	15,110	2,170	....
Belgium and Holland .....	8,500	250	....
Italy .....	4,640	140	....
North America.....	35,670	5,200	115,245
Scandinavia.....	550	50	....
Denmark .....	1,794		
Spain, Portugal, etc.....	1,090	2,317	....
Other lands.....	....	....	58,262
	134,162	17,980	413,507

Very recently another deposit of potash salts has been found in the Wipper valley, near Sonderhausen, Germany, which promises to prove an important rival to the Stassfurt beds. Difficulty of transportation has thus far interfered with the utilization of the East Austrian potash deposits.

*Nitrate of Potash.*—Extensive beds of this valuable material are claimed to have been found in Mashonaland, near Mt. Darwin, in the direction of the Hunyani river, by Mr. Griffiths, engineer to the South African Co. They are said to be from three inches to twenty feet in thickness and to underlie twenty square miles.

*Mineral Phosphates.*—The sources of the world's supply of phosphates with the amount furnished by each was estimated at the close of 1890 by Mr. Hermann Voss as follows :

	Tons.
England.....	20,000
Germany.....	40,000
Norway.....	20,000
Belgium.....	200,000
France.....	400,000
United States.....	600,000
Canada.....	30,000
West Indies.....	50,000
Other countries.....	100,000
	<hr/>
	1,460,000

Since then the Florida beds have been developed with extraordinary rapidity, and their output has increased from about 50,000 tons in 1890 to nearly 300,000 tons in 1892. But as this increment has been to a certain degree at the expense of other phosphate mining communities, especially under the combined influence of depressed business and diminished agricultural profits both at home and abroad, it is improbable that the total production of mineral phosphate for 1892 has largely exceeded 1,600,000 tons.

France enjoys the possession of phosphatic deposits of greater extent than any other European country, unless it be the undeveloped beds in Russia. They are practically of two sorts, those of higher grade and adapted for conversion into super-

phosphates (industrial), and those of lower types, which are ground and directly applied to the soil (agricultural).

According to *L'Engrais*, the estimate of May 1, 1892, of the French phosphatic deposits in the departments of Somme, Pas de Calais, and Aisne is as follows :

Area underlaid by deposits.....	185 hectares (457 acres)
Average yield per hectare.....	8,557 tons (French)

The quantity and quality are estimated at :

	Tons.
70-80 per cent. tricalcium phosphate.....	158,000
60-70 " " " " .....	222,500
50-60 " " " " .....	301,500
40-50 " " " " .....	428,500
30-40 " " " " .....	366,500
Total .....	1,477,000
25-40 per cent. phosphate chalk.....	636,500
Daily extraction from mines .....	955
Actual monthly production of works.....	29,125

The same authority has given the following estimate of the total productions of mineral phosphates for all France in the years 1891 and 1892.

	Industrial phosphates.		Agricultural phosphates.	
	1891, tons.	1892, tons.	1891, tons.	1892, tons.
Region Somme.....	278,000	407,000	56,000	52,000
Boulonnais Pernes-Cambresis, etc..	.....	.....	35,000	30,000
Ardennes .....	.....	.....	17,500	17,500
Meuse .....	.....	.....	45,000	45,000
Auxois .....	16,000	9,000	2,000	1,000
Indre .....	.....	.....	6,000	6,000
Region du Midi .....	12,000	10,000	3,000	2,000
Algerie et divers .....	2,000	2,000	2,000	2,000
Total .....	308,000	428,000	166,500	155,500

The French exportation and importation of phosphates for the years 1889-91 were as follows:

	1889, tons.	1890, tons.	1891, tons.
Exportation .....	150,963	122,002	91,246
Importation .....	6,914	21,452	17,069

The diminished exportation and increased importation during 1890-91 may have been due to the increasing activity of the Carolina and Florida phosphate mines in the same period.

*The Thomas Slag.*—The Thomas Slag has thus far defied my efforts to reach a satisfactory conclusion as to the extent of its agricultural use.

Hasenclever calculated the production of this article for 1891 as follows:

Production of	Thomas slag, tons.	Containing of phosphoric acid, tons.
Germany, Austria, and Luxemburg .....	617,600	105,000
England.....	178,700	30,390
France .....	84,500	14,360
Other countries.....	65,000	11,050
	<hr/> 945,800	<hr/> 160,800

While Rieman estimates the annual consumption of Thomas slag meal in Germany at 200,000 to 250,000 tons; Voss quotes it at over 300,000 tons; and other authorities at 450,000 tons. Recent commercial depression has reduced the output of the steel works, and consequently of the Thomas slag.

There is naturally great difference of opinion as to its agricultural value, although enormous quantities continue to be directly employed on German fields, and, that too, without interfering with the ever increasing application of acidulated and otherwise manipulated phosphates.

The report of the International Agricultural and Forestry Congress in Vienna (1891) on the availability of the Thomas slag, shows that the action of the Thomas meal is dependant on the amount of *matière noire* in the soil, which hastens the decomposition of the tetracalcium phosphate not only by its property of holding fast to moisture, but also by the influence of its ulmic and humic acids. Under favorable agricultural conditions it is necessary to employ only fifty per cent. more of the *active* phosphoric acid contained in the meal than is commonly used of water soluble phosphoric acid; but where the soil and conditions are not favorable, it is necessary to use two or three times as much. At recent prices of phosphoric acid in Germany, *viz.*, say, 2½ to 3 cents per pound for the active acid in Thomas meal, and six cents per pound for water soluble, there does not appear to be any great profit in the use of the meal instead of acidulated phosphates.

## THE FERTILIZER INDUSTRY IN GREAT BRITAIN.

The trade in commercial manures in the United Kingdom whether for home consumption or exportation, has necessitated large importations of crude materials and the erection of vast works for their manufacture. In 1889 there were registered in Great Britain 281 manure works, of all sizes; but among that number were eight of a capacity of 30,000 to 50,000 tons annually and twenty of 10,000 to 20,000 tons. The direction of these extensive plants has produced men of great business and scientific attainments; their operation gives employment to £5,000,000 of capital and thousands of workmen; their output serves to maintain the high fertility of British farms. In no other country have the effects of artificial manuring been so carefully studied; and wherever agricultural chemistry extends, thither the fame and achievements of the Rothamsted farm have spread.

The growth of the trade has fully kept up with that of other countries. The artificial manures manufactured in 1862 amounted to 200,000 tons, and in 1890 to 800,000 tons in addition to the sale of about 200,000 tons of nitrate of soda and similar manures (Voss).

The following table is very instructive as exhibiting the increment in the consumption of phosphatic material, whether in bones or mineral phosphates, as compared with the importation of guano. If the modern agricultural opinion holds good that the liberal application of nitrate of soda is almost imperative, but that it involves the greater use of phosphatic manures, whether it be that the former stimulates the leaching out of the phosphoric acid from the soil or that it causes the plant to assimilate more of the latter; in either case the tendency of the present day requires a greater employment of phosphates, and it is encouraged by an extraordinarily cheap market of those goods.

IMPORTATIONS INTO GREAT BRITAIN, ACCORDING TO THE BOARD OF TRADE RETURNS.

	1867.		1889.		1890.	
	Tons.	£.	Tons.	£.	Tons.	£.
Bones .....	83,814	457,436	62,435	308,212	69,949	372,048
Nitrate of soda .....	60,887	667,356	117,565	1,102,583	108,892	903,632
Phosphates .....	*	*	304,953	703,794	343,501	.....
Guano .....	192,308	2,109,506	28,604	199,783	28,005	167,181
Total .....	337,009	3,234,298	513,557	2,314,282	550,347	.....
Chemical manures exported. ....	.....	196,183	320,181	2,049,765	318,511	2,070,246

\* Non-assessed

IMPORTATIONS INTO GREAT BRITAIN, ACCORDING TO THE BOARD OF  
TRADE RETURNS.—*Continued.*

	1891.		1892.	
	Tons.	£.	Tons.	£.
Bones .....	82,945	416,849	63,008	286,452
Nitrate of soda .....	122,032	1,049,818	118,642	1,012,549
Phosphates .....	.....	.....	.....	.....
Guano .....	23,623	138,642	27,874	189,433
Total .....	485,372	.....	548,649	.....
Chemical manures exported.....	322,166	2,112,563	329,125	2,136,000

For first six months of 1892 importations of phosphates were .....146,156 tons.  
1893 .....154,328 "

The importation of phosphates into Great Britain has been as follows, according to the Anglo-Continental Guano Company:

Sources.	1888. Tons.	1889. Tons.	1890. Tons.	1891. Tons.
South Carolina.....	111,369	122,511	177,283	35,200
Florida .....	.....	.....	.....	96,881
English Antilles .....	11,010	1,880	3,970	1,960
Dutch " .....	10,736	14,730	11,763	8,851
Hayti and San Domingo	6,238	4,094	992	1,639
Venezuela and Guinea..	.....	.....	.....	540
Australia.....	.....	1,250	.....	.....
Canada.....	12,423	24,297	21,089	15,918
Portugal .....	6,979	1,326	.....	320
France .....	39,059	64,490	25,659	18,325
Belgium.....	54,261	64,643	82,096	70,723
Holland .....	4,137	2,210	2,428	3,434
Norway.....	.....	.....	4,151	1,495
Other countries.....	1,675	390	1,070	1,483
Total .....	257,886	304,953	343,501	256,769

*Exportations:*

To Sweden.....	.....	1,305	1,587	.....
" Germany.....	3,747	9,716	6,235	.....
" Holland .....	985	1,535	.....	.....
" Other countries.....	891	1,510	489	.....
	5,623	14,660	8,314	.....

The exportation of artificial manures from Great Britain for the year 1891, was as follows:

Countries.	Tons.	£ value.
To Germany .....	75,549	400,201
" Belgium .....	17,015	187,420
" France .....	43,651	275,016
" Spain .....	34,274	324,892
" West Indies.....	21,266	210,659
" Otherwise.....	130,411	714,375
	322,166	2,112,563

A material change has been induced in English agriculture by the development of the vast grain fields of the American North-



west. To-day England grows more clover, grass, and root crops, and less wheat, because of the greater profit in the former. Hence there is greater demand for phosphates and less for nitrogen (Voss).

*France.*—The annual importations and exportations of manures have been as follows :

	Importations.		Exportations.	
	1891. Tons.	1892. Tons.	1891. Tons.	1892. Tons.
Nitrate of potash.....	1,600	1,605	836	588
Nitrate of soda.....	180,278	205,887	6,501	7,673
Phosphates .....	17,644	41,185	91,821	83,885
Peruvian guano .....	2,999	.....	1,559	1,355
Other guano .....	1,990	3,427		
Acid phosphates ....	98,521	97,660	36,068	43,308
Chemical manures ...		21,462		14,655
Other manures.....	45,330	35,658	40,220	34,857

M. Joulie has reported to the Society of Agriculture of France the following table as the annual consumption of artificial manures in that country :

	Tons.
Nitrate of soda .....	215,000
Sulphate of ammonia.....	30,000
Natural phosphates (direct application)....	150,000
Thomas slag meal .....	70,000
Superphosphates .....	500,000
	<hr/> 965,000

France employs, additionally, potash salts to the value of 500,000,000 francs, and of other fertilizers to the value of 19,000,000 francs, making a total annual outlay of 120,000,000 francs, or \$24,000,000 (Joulie). The trade in commercial manures has trebled in the past twenty years.

*Germany.*—The importations of commercial manures for 1892 are as follows, according to *L'Engrais* :

		Tons.
Nitrate of soda .....		379,898
Sulphate of ammonia.....		34,206
Phosphates via Hamburg.	from Florida .....	48,928
	“ Canada .....	2,251
	“ South Carolina..	20,286
	“ Aruba .....	430
	“ France.....	6,181
	“ Belgium .....	1,340
	“ Norway.....	385
	“ Mexico .....	2,014
By other ports than Hamburg....	26,357	
By rail.....	150,000	248,172
<i>Carried forward</i> .....		<hr/> 662,276

<i>Brought forward</i> .....	662,276
Bone ash .....	14,620
Bone black refuse .....	10,973
Bone flour.....	24,551
Phosphatic guano .....	12,528
Nitrogenized " .....	3,665
Fish .....	5,458
Meat.....	5,937
<b>Total</b> .....	<b>739,108</b>

A conservative estimate of the consumption of artificial manures in Germany gives the following results:

	Tons.
Acid phosphates.....	450,000
Thomas slag meal .....	300,000
Bone meal, etc. ....	75,000
Precipitated phosphate .....	5,000
Nitrate of soda .....	250,000
Sulphate of ammonia .....	50,000
Potash salts .....	200,000
	<hr/>
	1,330,000

By others the consumption of acid phosphates is placed at 600,000 tons; of Thomas slag meal at 450,000 tons; of nitrate of soda at 300,000 tons; thus aggregating a total of at least 1,500,000 tons annually.

M. Maizieres (*L'Engrais*, 18th of August, 1893) estimates the average production of acid phosphates in Europe as follows:

	Tons.
France .....	440,000
England .....	500,000
Belgium .....	275,000
Germany.....	550,000
Holland, Sweden, and Norway.....	150,000
Italy and Switzerland .....	100,000
Other countries .	100,000
	<hr/>
<b>Total</b> .....	<b>2,115,000</b>

The production oscillates between 2,000,000 and 2,400,000 tons. It is derived from the consumption of about 1,000,000 tons each of mineral and other phosphates and sulphuric acid of 53° B.

*The United States.*—The consumption of commercial manures has grown very rapidly during the past twenty years in the

Atlantic, and especially the South Atlantic states. Their use is steadily on the increase in the central and gulf states. Gradually they are being sought after in the less distant and more thickly populated of the western ones.

In many of the states it is possible to obtain official figures as to the consumption of artificial manures within their borders, and I would herewith express my thanks to the many commissioners of agriculture and experimental station officers who have kindly assisted me in procuring the results given in the following table. I am also indebted to many friends who have given me estimates for the states that do not possess an official record of the quantity of commercial manures sold and used in them.

Consumption of commercial manures:

	Tons.
Vermont .....	4,000
Maine, New Hampshire, Massachusetts, and Rhode Island	40,000
Connecticut .....	20,000
New York .....	92,000
New Jersey (estimated)* .....	60,000
Pennsylvania .....	150,000
Delaware and Maryland (estimated)* .....	75,000
Virginia .....	140,000
West Virginia .....	15,000
North Carolina .....	145,000
South Carolina .....	200,000
Georgia .....	280,000
Florida .....	40,000
Alabama .....	90,000
Mississippi .....	25,000
Louisiana .....	15,000
Ohio .....	50,000
Indiana .....	35,000
Kentucky .....	12,000
Tennessee .....	15,000
Other states (estimated) .....	47,000
Total .....	1,550,000

\*Those marked as "estimated," have been given their quota by myself.

As the commercial center of the South Carolina phosphate deposits, and as the seat of probably the largest manufacture of phosphatic manures in this country or even in the world, the following figures as to the extent of the industry at Charleston—

which have been kindly gathered for me by an experienced manufacturer of that city—may prove interesting.

“The aggregate capacity of the Charleston fertilizer works when they are running full would be, say, 350,000 to 400,000 tons per annum. The incorporated capital of the works plus their surplus is about \$4,000,000. But this does not include the amount of money necessary for the companies to borrow in order to go on manufacturing, as the bulk of their capital is largely invested in plant. The borrowed money would vary in accordance with production and would be anywhere from three to seven millions. The sum of money expended for labor in a fair average year would amount to from \$350,000 to \$500,000.”

The world's consumption of commercial manures may be estimated at the following figures.

	Tons.
The United States .....	1,550,000
Germany .....	1,300,000
France .....	1,000,000
Great Britain.....	1,000,000
Belgium } (estimated).....	300,000
Holland } .....	100,000
Scandinavia (estimated) .....	100,000
Spain, Italy, and Austria .....	.....
	650,000
Total .....	5,500,000

Mr. Hermann Voss' table of the world's consumption of artificial manures arrives at a total of 5,400,000 tons, although differently arranged and distributed.

I will close my remarks with the preceding statement of what the fertilizer industry of to-day is contributing to the welfare of man. It is, truly for a suitable compensation, trying to feed and clothe him better, and to enable him and his posterity to continue to live at the old home instead of emigrating after having exhausted the fertility of his fields. I have endeavored to show to what extent the trade in commercial manures may be relied upon to meet these great exigencies.

## THE PREPARATION OF THE OAK TANNINS, WITH SPECIAL REFERENCE TO THE USE OF ACETONE AS A SOLVENT.<sup>1</sup>

BY HENRY TRIMBLE AND JOSIAH C. PEACOCK.

THE usual method for preparing a tannin from a substance as rich as nutgalls, or containing from sixty to seventy per cent. of the astringent principle, is to extract with a mixture of alcohol and ether, or, what amounts to the same thing, official ether, sp. gr. 0.750. When, however, the material is an oak bark, containing from four to fifteen per cent. of tannin, the choice of a proper solvent becomes a more difficult matter.

During the past year a number of experiments have been made on oak bark with a view of determining the most satisfactory solvent for the tannin. The following are especially worthy of consideration:

- (1) Official ether sp. gr. 0.750, which is equivalent to a mixture of alcohol and ether.
- (2) Acetic ether.
- (3) Water.
- (4) Acetone.

The greatest objections to ether are its expense and the slowness of its solvent action, which consume time as well as a large amount of menstruum.

Acetic ether is a much better solvent, and the expense is the chief difficulty in the way of its use.

Water is slow in its solvent action; this, however, is in part overcome by long maceration, and then slow percolation. The tannin must be separated from the resulting aqueous solution, either by agitation with acetic ether, or by precipitation with lead acetate. In the latter process it was found possible at a considerable sacrifice of oak bark to procure a quantity of light colored tannin, by precipitating one-half of the aqueous percolate with lead acetate, collecting the precipitate, stirring it through the other half of the percolate, and then filtering. The

<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

filtrate was very light in color, and was either evaporated under reduced pressure and submitted to further purification to be described hereafter, or it was agitated with acetic ether, and, after removal of the latter solvent, purified in the same manner.

Apart from the slowness of the process, the yield of tannin after purification was always small when water was used as a solvent.

Within the past few years acetone has appeared in commerce in a nearly pure form. Its solvent action has been suggested for several plant principles, but thus far little, if any, reference has been made to its use as a solvent for tannin, although there is good reason for believing that some manufacturers are using it for the extraction of nutgalls. It is cheaper than ether, but more expensive than alcohol. It is a better solvent of tannin than either of these, and extracts the tannin with less sugar and other carbohydrates, because of its poor solvent power over these. Its low boiling point,  $56.5^{\circ}$ , renders its recovery easy and rapid, without danger of decomposition to the tannin.

From a sample of powdered nutgalls, commercial ether extracted 59.77 per cent. of solids, while acetone extracted 62.24 per cent. of the same.

The following process, after some preliminary experiments, has been devised and thus far proven satisfactory:

The powdered oak bark was well moistened with acetone, packed in a glass percolator, and the menstruum poured on until it commenced to drop from the lower orifice, when the latter was closed with a cork, and the bark allowed to macerate for forty-eight hours. Enough of the solvent was poured on before maceration commenced to keep a thin layer of it above the drug. A glass plate smeared with petrolatum was kept on top the percolator to prevent evaporation. At the expiration of the maceration period, the stopper was removed and the percolation continued rapidly until the number of liters of percolate amounted to one-half the number of kilograms of oak bark used. The latter was then usually found to have been exhausted. In some instances a No. 20, in others a No. 40 powder, was used. In every case the acetone rapidly penetrated the drug and accomplished complete exhaustion.

The acetone was removed by distillation, the first portion on a water bath, under ordinary conditions, but the last portions by the additional aid of reduced pressure. The residual product was a dark red or brown semi-solid extract. This was warmed with water until nearly all of it dissolved. After cooling the whole was filtered and the clear filtrate was diluted with water so long as precipitation took place. This dilution separated much of the anhydrides. The filtrate from these was of a clear red color and yielded no further precipitate on the addition of water. It was then agitated successively with acetic ether. The acetic ether portions were mixed and the solvent recovered by distillation under reduced pressure, which yielded the tannin in a porous or "puffed up" condition. The product was then treated with cold water, and, after filtration, was again separated by agitation with acetic ether. This process was continually repeated until the tannin was readily and completely soluble in water. The tannin then possessed considerable odor of acetic ether, which was removed by solution in official ether, sp. gr. 0.750, and, after filtering clear, distilling off the solvent under reduced pressure. The product was then digested with absolute ether, which dissolved the small amounts of adhering resin and crystalline principles which occur along with it in the bark or result from decomposition when working it, and the tannin remained behind nearly pure, and readily and completely soluble in water.

This process was carried out on barks from the following species of oaks: *Quercus alba*, *Q. coccinea* and its variety *tinctoria*, *Q. falcata*, *Q. palustris*, *Q. Prinus*, *Q. bicolor*, *Q. stellata*, *Q. Phellos*, and *Q. rubra*.

It was found in some cases that by dissolving the acetone residue in a mixture of four parts water and one part alcohol, instead of water alone, there was less formation of anhydrides.

A few trials were made with a modification of the purification process in which the first acetic ether residue was dissolved in water and filtered through a freshly prepared lead compound obtained by precipitating a portion of the aqueous solution of the bark with lead acetate.

In some instances the resulting filtrate was nearly colorless,

but the loss of tannin was such as not to warrant the adoption of the process for general use. It might, however, be applied in certain cases with satisfactory results. From the colorless filtrate the tannin should be removed by agitation with acetic ether, and the remainder of the general purification process then carried out.

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### MILK, SKIM MILK, AND WHEY; A STUDY OF THEIR COMPARATIVE COMPOSITION AND SPECIFIC GRAVITY.

BY C. B. COCHRAN, WEST CHESTER, PA.

THAT the specific gravity of a milk is dependent upon the composition of the milk and varies according to the per cent. of each constituent is generally admitted. Upon this fact is based Richmond's extended formula. Having given the specific gravity, total solids, and ash of a sample of milk it is possible to calculate by means of this formula the percentage of fat, proteids, and sugar.

The formula is as follows:  $P = 2.8T + 2.5A - 3.33F - 0.7\frac{G}{D}$  ( $P$  = proteids;  $T$  = total solids;  $A$  = ash;  $F$  = fat;  $D$  = density, water at 60°F being taken as one; and  $G = 1000D - 1000$ ). From this formula Richmond calculates that each gram of proteids in 100 cc. of milk raises the gravity 2.57°; or that the density of the proteids of milk in solution is 1.346.

Dr. Duprè has found by direct experiment that one per cent. of casein raises the specific gravity of milk 2.55°, or that the density of casein in solution is 1.34.

Mr. Hehner by a different method of investigation concludes that the specific gravity of casein in solution is 1.3106.

From this figure as its density in solution, we conclude that each per cent. of casein raises the gravity of milk 2.36°.

I have recently made a comparative study of the specific gravity and composition of milk and the whey obtained therefrom. One of my objects in this work was to obtain data for determining the effect of each per cent. of casein on the specific gravity of milk and the density of casein in solution.

The following table shows the results of my work:



	Specific gravity of milk.	Total solids of milk.	Solids not fat of milk.	Specific gravity of whey.	Total solids of whey.	Casein removed	Effect on specific gravity of one per cent. casein.	Density of casein in solution.	Effect on specific gravity of whey of one per cent. total solids.
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
1.....	1.035	9.27	9.13	1.028	6.62	2.51	2.83	1.394	4.23
2.....	1.035	9.27	9.13	1.0266	6.1	3.03	2.80	1.390	4.36
3.....	.....	.....	.....	1.0266	6.1	0.52	2.69	1.370	4.36
4.....	1.0291	14.05	8.35	1.0285	6.62	2.33	2.78	1.386	4.30
5.....	1.0291	7.71	7.61	1.0249	5.98	1.63	2.63	1.358	4.16
6.....	1.0338	8.91	8.71	1.0282	6.50	2.21	2.62	1.355	4.34

In order to avoid as far as possible the influence of the fat, separator skim milk was used in all those analyses that were made to furnish a basis for determining the effect of casein on specific gravity. In the calculation allowance was made for the effect of the small amount of fat still remaining in the skim milk.

The method of work was as follows: Having determined by analysis the total solids, fat, solids not fat, and specific gravity of a sample of skimmed milk a few drops of a strong solution of rennet, or acetic acid is added to about one pint of the milk in a flask which is then tightly corked and stood on a water bath until coagulation has occurred and a clear whey separated.

After thorough cooling the whey is filtered and if clear the total solids it contains and specific gravity determined. The difference between the total solids of the whey and the solids not fat of the skim milk is taken to represent the casein removed. Divide the difference in specific gravity between skim milk and whey by per cent. of casein removed and the quotient represents the loss of specific gravity due to removal of one per cent. casein. The density of casein in solution is now found by the formula  $D - D' = \frac{1-x}{100} x$ ;  $D$  = specific gravity of whey;  $D'$  = specific gravity of skim milk, minus all fat;  $x$  = effect of one per cent. curd on density.

By this method of work the numbers in columns 7 and 8 were obtained. The average of these results shows that each per cent. of casein removed lowers the gravity of the solution 2.72 degrees; and that the density of the casein in solution is 1.376.

The solids coagulated by rennet freed from fat were found to contain 1.08 per cent. ash. All the remainder is regarded as casein or proteid matter. The disturbing influence produced by the removal of so small an amount of mineral matter with the casein would have only a very slight influence on the specific gravity. Moreover if this mineral matter is combined with the proteids as they exist in the milk it is proper that it should be considered as a part of the proteid matter in determining its density in solution.

The results obtained vary much more than I like to see. I am unable to explain the cause of the variation in the results here obtained. The specific gravity was obtained in all cases by weighing in a specific gravity flask furnished with side tube and cap. The solids were obtained by drying on asbestos fiber. The sugar of the residue from whey very easily caramelizes on drying, and for this reason it is more necessary to use an absorbent like asbestos for whey than for milk.

Having determined specific gravity and total solids of a large number of samples of whey, I conclude that when the coagulation is properly performed under similar conditions, the specific gravity, and total solids of whey of pure milk will vary within quite narrow limits. I find the specific gravity to be 1.027 or higher and in all but one case as low as 1.0285. The total solids vary between 6.5 per cent. and 6.9 per cent. If a sample of whey be reheated, further coagulation will take place. In this way the specific gravity of a whey was reduced from 1.028 to 1.0266.

A milk that had been allowed to decompose for a period of twenty days furnished a whey that had a specific gravity of 1.0255. The whey had an acidity corresponding to 0.76 per cent. of lactic acid. The lowering of the specific gravity was a natural result of the fermentation.

If the number representing the specific gravity of the whey above 1000 be divided by 4.25, the quotient represents fairly well the per cent. total solids contained in the whey. For example a whey of sp. gr. 1.028 will contain  $28 \div 4.25 = 6.59$  per cent. total solids.

As might be expected I find the whey of any given milk has

the same composition no matter whether it is taken from the original milk, the cream, or skim milk. This being the case a knowledge of the variation in specific gravity and composition of whey of pure milk may be of value in determining adulteration, especially when the milk comes into the hands of the analyst in a churned or soured condition. It is also equally valuable in testing cream for added water.

The following table illustrates the value of the whey test in this particular. It shows the specific gravity of the whey in comparison with the composition of milk and cream both in pure and watered samples:

Numbers.	Specific gravity.	Total solids.	Solids not fat.	Specific gravity of whey.	Total solids of whey.	
1 .....	1.0307	14.32	8.78	1.028		A partially creamed sample of milk.
2 .....	1.0315	12.05	8.55	1.027		Poor milk.
3 .....	1.0273	10.90	7.50	1.023		Watered milk.
4 .....	1.0204	12.05	6.15	1.0213		Watered cream.
5 .....	1.0318	14.68	9.49	1.0255	5.89	Whey separated after milk had
6 .....	1.031	12.05	8.45	1.028	6.59	stood three weeks.
7 .....	1.0312	12.45	8.55	1.027	6.35	
8 .....	1.032	12.90	8.80	1.0275	6.47	
9 .....	1.0329	13.22	9.02	1.0273	6.42	
10 .....	1.0324	12.98	8.88	1.0283	6.66	
11 .....	1.0329	12.40	8.90	1.027	6.35	
12 .....	1.0278	8.81	8.71	1.0234	5.50	Watered skim milk.

In closing this article I desire to call attention to Hehner and Richmond's original formula, which is expressed in a working form in Richmond's milk scale. Does this formula express the true relation existing between the fat, solids not fat, and specific gravity of a milk? Or is it possible to establish any such relation? So far as I know this formula has never met either the approval or disapproval of American chemists in any authoritative way. Chemists of repute oftentimes report very different results on what I believe are fair samples of the same milk. This difference is largely due to different methods of work, and as a consequence the results in one or both cases are incorrect.

I have had much experience with Richmond's milk scale, using it as a check in analytical work, and am very favorably impressed with its accuracy. If this formula or some other one

should receive authoritative approval as a check in the analysis of normal milk it might assist in establishing the adoption of similar methods of analysis or at least in methods that gave concordant results, and would serve to correct faulty analyses.

In case the chemist obtains results not in accord with the formula which may be chosen let him regard it as necessary to investigate the cause of this disagreement.

Such a course would prevent loss of public confidence in milk analysis which at present is likely to occur.

### IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.<sup>1</sup>

By G. DE LAIRE AND FERD. TIEMANN.

Received September 8, 1893.

**I**N the dried rhizomes of iris florentina we have discovered a new glucoside of peculiar composition and remarkable properties. It is prepared as follows:

The alcoholic extract from ten kilos of powdered iris root is stirred with two liters of lukewarm water and one liter of a mixture of acetone and chloroform of 0.950 specific gravity.

If allowed to stand quietly the liquid separates into two layers, a lower aqueous solution of grape sugar, organic acids, coloring substances, etc., and an upper acetone-chloroform solution containing the substances of the alcoholic extract insoluble or only slightly soluble in water.

The glucoside extracted from the root by means of the alcohol swims in the dark-colored syrup in amorphous white masses. The two layers are separated by decantation, the white flakes collected on a filter, washed with a little hot water and dried at 100°. The white powder obtained in this way was washed with ether and light petroleum to free it from adhering impurities and crystallized from boiling dilute alcohol (one volume ninety per cent. alcohol to two volumes water). We call the substance obtained in this way

*Iridin* ( $C_{24}H_{36}O_{13}$ ). It forms fine white needles which become yellow in moist air and melt at 208°. It dissolves scarcely at all in alcohol, somewhat more easily in acetone. At ordinary

<sup>1</sup>This paper was intended for the World's Congress of Chemists, but arrived too late for presentation.

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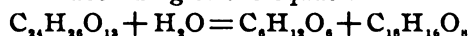
temperatures one liter of alcohol dissolves about two grams, one liter of acetone about thirty grams. The substance is insoluble in ether, ethyl acetate, benzene, and chloroform, but dissolves easily in hot alcohol. Chloroform precipitates it from its solution in acetone, and the mixture of acetone and chloroform of 0.950 sp. gr., which we used in its preparation, dissolves only five grams per liter. At ordinary temperatures iridin is not attacked by dilute mineral acids. By the action of aqueous alkaline solutions deep yellow solutions are obtained from which, after a short time, the unchanged substance can no longer be separated by acids.

Iridin has the composition expressed by the formula,  $C_{11}H_{12}O_{11}$ .

## ANALYSIS.

	C.	H.
Calculated percentage .....	55.17	4.98
Found.....	55.06, 55.23, 55.19	5.25, 5.27, 5.47

By means of dilute alcoholic sulphuric acid, iridin is decomposed at  $80^{\circ}$ – $100^{\circ}$  according to the equation



into grape sugar and a well crystallizing substance which we call irigenin.

To effect this decomposition a mixture of thirty parts glucoside, thirty-five parts water, three parts concentrated sulphuric acid, and forty-five parts alcohol is heated in pressure flasks for five to six hours on the water bath with occasional shaking. The liquid is decolorized as far as possible with animal charcoal and set aside to crystallize. The largest part of the irigenin soon separates as yellowish crystals; the rest crystallizes out after the alcohol has been driven off by a current of steam. The average yield of irigenin was sixty-five per cent., while theory requires 77.77 per cent.

The glucose is found in the liquid filtered from the irigenin, which contains also all the sulphuric acid used for the decomposition. This is removed by boiling with barium carbonate and the filtrate evaporated. The syrup so obtained solidifies after standing several weeks in crystals which are purified by recrystallization from methyl alcohol. We find the melting point of the anhydrous crystals to be  $145^{\circ}$ , of its osazone  $205^{\circ}$ . The

aqueous solution of the sugar is dextro-rotatory and shows birotation. Using boiled solutions we obtained

$$\begin{aligned}[a]_D &= 8.11^\circ \text{ at } 20^\circ \\ c &= 7.052, l = 220 \text{ mm.}, \\ \text{and sp. gr.} &= 1.0296, \\ \text{therefore } [a]_D &= 52^\circ 54'\end{aligned}$$

while according to Tollens formula  $[a]_D$  for a seven per cent. grape sugar solution is  $52^\circ 40'$ . The sugar is, therefore, *d*-glucose. We have found no other sugar in the syrup from iridin.

*Irigenin* ( $C_{18}H_{18}O_8$ ).—Irigenin may be purified without difficulty by repeated crystallization from boiling benzene. Water separates it from an alcoholic solution in distinct rhombohedra. The crystals melt at  $186^\circ$ ; alcohol, benzene, and chloroform dissolve it easily when warmed, ethyl acetate and chloroform at the ordinary temperature. It is, however, difficultly soluble in water and nearly insoluble in ether and light petroleum. It has the properties of a phenol. Even very dilute alcoholic irigenin solution is colored deep violet by ferric chloride solution. Alkalies dissolve irigenin but decompose it rapidly, which is made evident by the deepening color of the yellow solution. After a short time acids no longer precipitate from the alkaline solution an unchanged compound, but an amorphous precipitate.

#### ANALYSIS OF CRYSTALLIZED IRIGENIN.

	Per cent. C.	Per cent. H.
Calculated for $C_{18}H_{18}O_8$ ..	60.00	4.44
Found .....	59.79, 59.78, 59.48, 59.77	4.50, 4.48, 4.54, 4.46
" .....	60.27	4.13

The rise in boiling point by Beckmann's method with an alcoholic solution is in accordance with this formula.<sup>1</sup>

Irigenin contains two hydrogens easily replaceable by acyles, which indicates the presence of two hydroxyls.

<sup>1</sup> Beckmann's method for molecular weight determinations usually gives with compounds of complex composition like irigenin, using concentrated solutions, results which are too high. Under these conditions we have found the molecular weight one-fourth to one-third too high. In order to facilitate the dissociation of the molecular aggregates the solution may be diluted, with, however, a correspondingly smaller difference in boiling points. These vary too much with the use of the ordinary laboratory apparatus to allow one to obtain satisfactory figures for the molecular weight.



*Dibenzoylirigenin*,  $C_{18}H_{14}O_8(COC_6H_5)_2$ , was prepared by the Baumann-Schotten method by the action of benzoyl chloride upon a freshly prepared solution of irigenin in dilute alkali. It is necessary to work rapidly and at a low temperature so that the reaction may take place before the irigenin is decomposed in another way by the alkali. But the formation of by-products can not be entirely avoided. They are separated by repeated fractional precipitation from the benzoyl solution by means of light petroleum. The substance is finally recrystallized from alcohol and forms a white crystalline powder melting at  $123^{\circ}$ – $126^{\circ}$ .

## ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated.....	67.61	4.22
Found .....	67.08	4.40

*Diacetylirigenin*,  $C_{18}H_{14}O_8(COCH_3)_2$ , is easily formed by heating in a closed tube for three hours five parts irigenin with five parts melted sodium acetate and ten parts acetic anhydride. It separates in crystals when the viscous product of the reaction is diluted with water and neutralized with soda. The solution in chloroform diluted with much ether leaves on evaporation a white crystalline powder melting at  $122^{\circ}$ , which is easily taken up by hot alcohol, dissolves only slightly in ether and is insoluble in water and benzene. It deliquesces, however, immediately if a drop of chloroform is added. Light petroleum precipitates from the chloroform solution beautiful white plates which melt at  $82^{\circ}$ , and are a double compound of diacetylirigenin and chloroform. The greater part of the chloroform volatilizes when the crystals are allowed to lie exposed to the air for some time, but the melting point does not change. The analysis of the substance recrystallized from much ether and melting exactly at  $122^{\circ}$  has led to the following numbers:

CALCULATED FOR  $C_{22}H_{20}O_{10}$ .

	Per cent. C.	Per cent. H.
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Found .....	59.33	4.71

With reference to the determination of the number of replacing acetyl groups, we have saponified the acetyl derivative with



tures extract of hops by a new process. Carl Rach has a patent on the preparation of wort from Indian corn (500,294). Wm. E. Bradley has an improvement on the manufacture of whisky (499,316) and James A. Tilden patents a process of malting (500,305).

*Glue, etc.*—Michael A. Goloseieff utilizes gelatine refuse or broth from evaporating to 27°–28° B., adding quick lime, allowing mass to expand and dry, and grinding (500,100). Eduard Rauppach and Leopold Bergel heat a mixture of curds and water to 104° F., add an alkali to precipitate the casein, and after separating the latter, heat it with an alkaline solution to 90°–110° F., in their process for making glue (500,428).

*Paints and Varnishes.*—George H. Smith has a method for making varnish (496,451). Ludwig Pflug patents a paint for ships (496,895) which contains hydrazin and its salts, and W. N. Blakeman, Jr., has a process for utilizing metallic and earthy oxides and salts as pigments or paints (496,990), by combining with some salts capable of absorbing carbon dioxide when the pigments are applied. James E. and G. H. McAlpine use for a fire or water proof-paint, a mixture of coal tar, crude petroleum, benzine, resin, sulphate of zinc, sal-soda, and linseed oil (500,346).

*Plasters, etc.*—"Hydromagnesite, oxalic and boracic acids and mother liquor of sea water with sand, fiber and an oleaginous substance" is what Hugo Gallinowsky names as an artificial stone composition (500,485). Enos A. Bronson prepares a finish for plastering by mixing lime, gypsum, white sand, soapstone or talc, and china clay or kaolin with enough water to form a pasty mass, adding alum and borax, drying, grinding, and adding to the mass calcined gypsum and white sand (499,710). M. B. Church mixes gypsum with glue as it comes from the rendering tank without drying as a process for making "retarded gypsum" (497,947), and 497,948 is a process for manufacturing gypsum compounds, which consists in mixing the gypsum in a dry, pulverized condition, with the retarder in a hot liquid condition. George H. Blake uses "wood tar, rosin, and pulverized plumbaginous slate" as a composition for roofing (498,840), while A. Monroe incorporates the following for the same purpose: "Portland cement, sand, plaster of Paris, crude petroleum, turpentine, salt and water" (500,024).

*Organic Compounds.*—Prosper Monnet patents a process for making anisoline (499,927). Meinhard Hoffman patents his plan for forming naphthylene-diamin-disulpho acid (498,882), and 499,301 is a process for making derivatives of amido-crotonic acid, invented by L. Lederer.

*Miscellaneous.*—August Viner uses saltpeter, borax, glycerin, and water as a compound for glazing collars and cuffs (499,685), and "whiting, ammonia, kerosene oil, coal ashes and water" is what is claimed by Dora A. Smith for a silver cleaning composition (499,401). "Oil and sulphur boiled together, turpentine and salt," Walter E. Rohner combines for wood polishing (498,961). Carbon and tar pressed and baked in place

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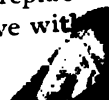
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### ON APPARATUS FOR PROMOTING THE INTERACTION OF LIQUIDS AND GASES.<sup>1</sup>

BY PROFESSOR GEORGE LUNGE, PH.D., OF ZÜRICH.

**B**OTH in theoretical and industrial chemistry one of the most frequent operations consists in the interaction between liquids and gases. On the laboratory scale this operation presents but few difficulties and is generally treated rather briefly, both in chemical literature and in laboratory teaching. Even here the matter is not quite so plain as is assumed by many chemists, and the success or failure of analytical operations is sometimes intimately connected with this question. Where the task is merely that of treating a liquid with a gas, irrespective of the quantity of the latter consumed, the question is certainly simple enough. But where it is required to completely absorb every trace of a special gas diluted with a large quantity of inert gases, the ordinary wash bottles and similar apparatus are mostly insufficient. I have made this matter a special study in connection with the estimation of nitric oxide in chamber-exit gases and similar difficult cases, and I have described the best shape of absorbing apparatus for such purposes in a communication to the *Zeitschrift für Angewandte Chemie*, 1891, p. 567, and in the *Journal of the Society of Chemical Industry*, 1890, p. 1015.

The task becomes far more serious when operations on the

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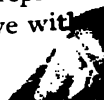
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dilute alkali, and titrated the acetic acid, separated after acidifying with sulphuric acid and distilling with steam.

We noticed beforehand that irigenin was decomposed by concentrated alkali with formation of formic acid. We determined, therefore, how much formic acid was produced by treatment of a quantity of irigenin equivalent to the diacetylirigenin used for the acetyl determination under exactly the same conditions and subtracted the value obtained from that given in the acetic acid titration. For our purpose the results so obtained are sufficiently near the truth, but under these difficult conditions results agreeing closely with theory are not to be expected.

ACETYL DETERMINATION.—CALCULATED FOR  $C_{18}H_{14}(C_2H_3O)_4O_8$ .

	Per cent. $C_2H_3O$ .
Calculated .....	19.37
Found .....	21.41

The compound melting at  $122^\circ$  is, therefore, diacetylirigenin.

(To be continued.)

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

**Zinc.**—Johannes Pfleger has an electrolytic process for zinc (495,637). It is described as consisting in adding a basic zinc salt solution to a zinc-containing anode, to which basic zinc solution a conducting neutral salt has been added. George T. Lewis treats roasted zinc sulphide ores by adding sodium nitrate or its equivalent to unite with the sulphur left, roasting to form soluble sulphate, leaching out, oxidizing the zinc in the ores thus freed from sulphur and collecting the zinc oxide fumes (495,593). G. M. Gouyard concentrates zinc bearing sulphides by roasting the ores, and at the final stage employing a low heat, adding a small per cent. of finely pulverized coal in a reducing atmosphere, which renders the iron present magnetic and precipitates the lead on the iron, and then separating the iron with a magnetic separator (495,550). Zinc oxide is prepared by the method of Carl V. Petraeus from sulphide ores by subliming the zinc, reducing the temperature of the gases and zinc oxide driven off below a bright red heat, catching the zinc oxide fumes, and finally heating at a red heat to whiten and free from sulphur compounds (496,205). W. R. Ingalls and Francis Wyatt treat complex ores as follows: First, roast to convert into sulphates, recovering sulphur driven off as sulphuric acid; next, lixiviating with water and said sulphuric acid, removing iron if necessary, precipitating zinc as carbonate or basic carbonate, using sodium carbonate, and burning to zinc oxide,



such tiny basins. Each of these is provided with a central hole differing in width from less than a quarter to half an inch, according to circumstances. The top of each hole is surrounded by a slightly raised margin about a sixteenth of an inch deep. The plates are made on two different patterns, in one of which the basins are distant from the edge by half the width of a basin, whilst in the other pattern they come right up to the edge. Consequently when these two patterns of plates are superposed over one another, the holes in each plate correspond to the center of the cross formed by the ledges of the four basins just above and below. Hence when a liquid is run upon the plates each of the tiny basins is filled independently up to the edge of the margins round the holes. It then overflows through the hole and the drop thus formed falls upon the cross of ledges underneath, and is scattered over the four corresponding basins. Furrows on the bottom sides of the plates prevent the drops from running along the bottom and falling down in other places than those where they are intended to get to. While in this manner the liquid is spread on each plate in a thin film, which is constantly renewed by drops from above in the most regular manner, the gases are just as regularly divided, and issue in about 1000 jets through each plate without the possibility of any false channels being formed which so frequently occur in coke towers. As the gas jets ascend through the holes in any one of the plates, they strike against the solid portions of the plate next above, and are thus deflected from their course and constantly mixed over again. All this will be more completely understood by looking at the diagram.

It is easy to see that ordinary pottery, even of the best known makes, will not stand in this case. The plates must be very thin and at the same time they must be absolutely level and true in all parts. They must also bear a certain mechanical strain and sudden changes of temperature together with complete resistance to the action of chemicals. I did not know of any chemical pottery in Europe which fulfilled these conditions as well as that of Mr. Rohrmann, and for that reason I associated myself with him in that matter. I am glad to say that the large specimens of his plates submitted to the London and

Liverpool meetings of the Society of Chemical Industry by buyers of the same have excited universal admiration there.

Where no metal, not even lead, can be tolerated, the plates are made of circular shape and are built up with stoneware rings to keep them in proper distance, in stoneware pipes, thus forming columns of circular section and containing up to forty plates or even more. The sectional area of these columns is limited by the practicable width of the stoneware pipes and does not generally exceed two feet six inches. Large streams of gases, for which such a section would not suffice, have to be sub-divided among two or more columns. Where, however, lead is not excluded, the plates are made square, and are combined by means of specially designed bearers in such manner that any sectional area can be produced, the whole being enclosed in a leaden shell. The bearers support each plate independently of the others, and cover the whole of the lead so as to protect it entirely against the action of the heat and even of the chemicals, so that this system might be employed even in such cases where unprotected lead could not be employed.

Plate towers of these two constructions have now been proved to be, size for size, probably the most efficient apparatus hitherto invented for bringing gases into intimate contact with liquids, except in such cases where there is some solid or tarry matter present which would obstruct the holes and fill up the small basins. In all other cases the plate towers are from ten to twenty times as efficient as an equal space of the best arranged coke towers; and when they are compared with empty spaces, such as vitriol chambers, their efficiency is found to be hundreds of times greater than that of those spaces. From the nature of the case, plate towers can not be made of cheap materials turned out at a low price, but they are after all far cheaper than other apparatus with which they enter into competition, and would be so, even if their initial cost were equal to that of the coke towers or vitriol chambers they replace, seeing that they require next to no space, foundations and buildings, and that there is no pumping of liquids to a great height.

I now beg permission to illustrate my assertions by a number of examples taken from practical cases. I shall not touch upon

some applications which may ultimately become very important indeed, such as the manufacture of acetic acid, but I shall confine my remarks exclusively to the application of plate towers in the manufacture of the so-called heavy chemicals, that is, sulphuric, hydrochloric, nitric acid, and chlorine.

The application of the plate towers in the manufacture of sulphuric acid takes place in three different ways, as a partial substitute for the Glover towers, as a partial or entire equivalent of the Gay Lussac tower, and as a partial substitute for the vitriol chambers themselves, enabling a set of chambers to produce up to sixty or seventy per cent. more acid than without the plate towers. I shall quote practical instances for all three applications.

As far as the Glover tower is concerned, it stands to reason that it can not be entirely replaced by a plate column, and that for two reasons. In the first instance, the quantity of dust carried over from the pyrites, or even sulphur burners, is so great that the plates at the bottom of the tower would soon be choked up. Secondly, the temperature of the gases entering at the bottom and that of the acid descending in the tower is too different to expect any kind of pottery to stand the inevitable sudden changes and inequalities, at least in ordinary cases. Where, however, both these objections are done away with by a previous utilization of the burner gases for concentrating acid in lead or platinum dishes, as in Henry Glover's plan ("Sulphuric Acid and Alkali," second edition, 1, p. 201), the whole Glover tower might be made of a plate column. In the ordinary towers, however, the bottom part will have to be packed in the usual way with a network of bricks, or flints, or cylinders, while the upper part is filled with my plates. Or else the same plan may be adopted which has been applied with full success by Dr. Petri at the Buchsweiler works in Alsace. There they burn spent gas oxide containing, besides free sulphur, some ammonia salts, part of which is not removed by washing and exerts a destructive influence in the niter in the Glover tower. This well-known reaction by which the nitrogen of both the ammonia and the nitrous vitriol is set free as such, takes place only at high temperatures. Reasoning from

this, Dr. Petri put on the top of his ordinary Glover tower a small plate column, consisting of thirteen layers of two plates each. The gases issuing from the Glover tower enter this small column at a temperature of  $90^{\circ}$  and leave it at  $60^{\circ}$  C., while the fresh nitrous vitriol is run in at the top and runs away at the bottom in order to feed the Glover tower. In this small column, holding altogether forty cubic feet, eighty per cent. of the denitration takes place, for which an ordinary Glover tower of eight by eight by twenty-five feet, equal to 1,600 cubic feet, is generally provided, leaving only twenty per cent. of the denitration to the Glover tower and effecting the denitration at such a low temperature that the ammonia exercises no injurious action. The contrast between the efficiency of those forty cubic feet of plate tower and the 1,600 cubic feet of ordinary Glover tower space is certainly startling. If, by the way, some of the plates should crack, they would all the same remain in their places and perform their work nearly as well as before.

The action of the plate column as a Gay Lussac tower is illustrated by an American works where a set of chambers of 212,000 cubic feet is provided with a plate tower of twenty layers of ten plates each. This tower, possessing about 280 cubic feet of active space, now fulfills the function of a coke tower of about 4,000 cubic feet. But it is evidently too wide for its present work, and hence requires too much acid for feeding it equally all over. It is hence intended to pass the gases from another set of 123,000 cubic feet through it, and it is expected that it will be equal to this as well, in which case it would act like about 7,000 cubic feet of ordinary coke-tower space, that is, twenty-five times its cubic capacity.

A very important advantage of the plate tower over the ordinary coke tower is the chemical indifference of the former to all the gases concerned, whereas the coke, as I have repeatedly proved, acts as a reducing agent upon the nitrous compounds and causes a loss of niter together with a gradual crumbling of the coke packing, while a plate tower lasts practically forever.

Another advantage of the plate column is its inconsiderable height, which not merely makes the pumping of the absorbing

liquid much easier than with the ordinary coke tower, but in some cases admits of altogether dispensing with pumping. Thus, at the last-mentioned works the nitrous vitriol runs from the bottom of the plate tower serving as a Gay Lussac tower upon the top of the Glover tower, the former being placed at a convenient height for that purpose. This would have been impossible if the Gay Lussac had been an ordinary fifty or sixty foot coke tower. The matter might have been arranged just as easily in the opposite way.

The most important and interesting application of the plate column in the manufacture of sulphuric acid is that for diminishing chamber space. Every theory of the lead chamber process, worthy of such a name, supposes a constant interaction of the gases and the liquid portions floating in the chamber atmosphere in the shape of mist. Before that action is completed in the ordinary lead chambers, the ingredients must remain a very long time in contact with each other, and must quite gradually cool down, principally owing to the fact that the particles of the mist are separated by comparatively wide spaces and the action of the water or dilute acid on the nitroso-sulphuric acid is thereby greatly retarded. This drawback had been more or less clearly recognized by many previous inventors, beginning with Gossage, and many endeavors had been made to overcome it. But all these had either completely failed or at least effected their purpose so incompletely that they had been given up again. Thus all proposals for employing coke within the chambers for improving the mixture of the gases have necessarily broken down in consequence of the chemical action of the coke referred to above. Mechanical aspiration of the gases and re-injecting them into the chambers has also failed to improve matters to a great extent. Some little time ago the Thyss process attracted much attention. In this lead towers are interposed between the chambers, filled with lead sieves, but, as might have been foreseen, the lead sieves were soon stopped up by lead sulphate and quickly destroyed. The Delplace chamber is another attempt to produce a better mixture of the gases, but it can not attain this end at all completely or much better than any lead chamber of the old type.

By adapting my plate column to this special end, I believe, I have solved the problem more efficiently than any of my predecessors. I based my proposal on the fact, first securely established by myself, together with Dr. Naef, that the rate of formation of the acid within the first chamber of a set is very unequal. This was proved by very numerous observations and analyses, carried on at a Swiss works for several months, and afterwards confirmed at other places by a number of entirely independent observers. The curve of acid formation rises rapidly to a certain height, but about midway in a 100-foot chamber it flattens and turns nearly to the horizontal, so that the second half of the chamber performs very little work indeed. But as soon as the gases pass over into the second chamber, the formation of sulphuric acid is suddenly revived, thus proving that the contact of the gases and vapors with the end wall of the chamber, and their compression in the connecting pipe exerts a very favorable influence on their interaction. Most probably several conditions are at work here. The shock of the vapors against the solid surfaces, by which the sundry particles forming in their separation a fog or mist are brought together and are made to interact; further, the better mixture of the gases during their passage through the narrow connecting pipe, and lastly the cooling action of the end wall of the chamber, which cooling, according to the modern theories of the vitriol chamber process, is essential for the production of sulphuric acid from its components. Having thus, as I believed (and I think justly) recognised the causes of the favorable influence exerted by dividing the chamber space into several chambers, and of the revival of the reactions distinctly observable between the first and the second chamber, I proceeded to draw the consequence of these views, by immensely multiplying the conditions found to be conducive to the acid forming process. For this purpose I interposed, like Thyss, a kind of tower between the first and second chamber; but in lieu of simple lead sieves, which produce only an incomplete mixture, and which, as noticed before, are doomed to rapid destruction, I filled my tower with the plates I had previously devised for other purposes, consisting of chemically in-attackable material, and by their geometrical design solving in

the completest possible manner the problem of thoroughly dividing the gaseous current, and intimately mixing up its ingredients, together with innumerable shocks against solid surfaces. Even then two conditions for a proper chamber process would be absent, *viz.*, the supply of sufficient moisture, and the keeping down of the temperature below the optimum for the process; and these two conditions I supply simultaneously by feeding the towers with more or less dilute acid, whose evaporation yields both the water and the cooling action necessary for compelling the reaction to take the best possible course.

Theoretically there is no reason why such columns should not take the place of the lead chambers in their entirety. Long ago similar plans have been proposed, and quite recently a Mr. Barbier has again taken out a patent for a system, in which sulphuric acid is made without any lead chambers, in towers filled with earthenware cylinders, and fed with acids of different strength. In principle Barbier's plan does not at all differ from others which have been tried ten or twenty years ago, and have failed. Just that failure, I must confess, has discouraged me from proposing the entire abolition of the lead chambers to other people; but if I possessed a chemical factory of my own, I should certainly have tried that plan with my plate towers three years before Barbier took out his patent, which, of course, cannot be applied to that well-known principle, but only to his special kind of towers. For the present, at any rate, I do not venture to go beyond proposing to cut off the chambers at that point where all observations have proved the reactions to decrease rapidly in intensity, say, at a length of fifty feet, and to replace the remaining length of an ordinary chamber by a plate tower, repeating this arrangement with the second, and if needful with the third chamber of a set.

Up to this time no chamber system has been fitted up according to the plan just described, but in all cases the plate towers have been put between the existing chambers of an ordinary set, where they certainly perform a great deal of work, but evidently much less than could be done with a more perfect arrangement. I have therefore the right to consider the results hitherto obtained as a minimum; and looked at in this light, they are extremely

encouraging, as far as I have been able to ascertain them, in which aim I have been much hampered by the unwillingness of many manufacturers to supply information for the benefit of their competitors. Thus for instance, the United Alkali Company, in England, has erected a plate tower, but I have not been able to extract any information as to the works at which that has been done, and for what purpose, let alone telling me anything about the results obtained therewith. In a few cases, fortunately, I have been favored with more information, and this I will now lay concisely before you.

At a Bohemian works, the first where this plan has been adopted, and where, consequently, the best conditions were not yet ascertained, the plate column has raised the quantity of pyrites burnt to an additional thirty per cent. Beyond this it is impossible to go in that place, as there is no more room in the kilns; but as the chamber following the plate column has no work whatever left to do, the acid making process having been completed in the column, the real increase of chamber capacity has been seventy per cent.

At a Dutch acid works there are two sets of chambers of exactly the same dimensions, namely one chamber of 64,400 cubic feet, and another of 19,950 cubic feet following this. In one of the two sets a plate column of ninety-six plates in all has been placed between the two chambers, and this set, I am informed, can be worked as if it held 22,500 cubic feet more than the other, so that each of the ninety-six plates would correspond to a space of 234 cubic feet, that is, more than two hundred times the room occupied by the tower itself.

At Valencia, in Spain, a plate column had been working for eighteen months, when I received the last news about it. That set was then burning forty-two per cent. pyrites in excess of what it had burnt before it had been provided with the column, whilst the consumption of niter had diminished from 2.2 down to 1.7 parts to 100 of fifty-two per cent. pyrites, which signifies a saving of nearly twenty-five per cent. of the niter. The yield of acid is excellent, and could hardly be better in that hot climate, where the first chamber in summer has a temperature



up to 88° C. In the plate column it comes down to 28° or 50° C., and the gases go into the Gay Lussac with 40° C.

Looking at the very imperfect way in which the plate towers have been hitherto adapted to old sets of chambers, it is fair to hope that much better results than even those which I have been able to report would be obtained, if that principle were more thoroughly carried out. Even the present results show an immense superiority over Barbier's system, which, according to his own statement, requires one-sixteenth of the present chamber space, whereas my columns do from 100 to 250 times as much work as the same cube of chamber space. The reason of this great superiority evidently lies in the scientific construction of my plates, compared with the hap-hazard packing of other systems.

Allow me now to say a few words on the employment of plate towers for the condensation of hydrochloric acid. The very first tower which I designed was tried for this purpose, and the experience gained in that trial was utilized for a thorough reconstruction of the system. Since that time several plate towers have been supplied for the same purpose, and a very large one has been delivered just before my leaving Europe; but all information on the subject has been withheld from me, so that I cannot communicate anything on that subject beyond what was observed at the first trial, mentioned above, with the very imperfect kind of columns first used, at the celebrated Griesheim works, one of the most carefully managed alkali works in the world. According to the official report then furnished to me, the following results were obtained. Two superposed columns, of sixty cubic feet each, with a total plate surface of fifty-six feet (reckoning both top and bottom side of the plate) effected the condensation of ninety per cent. of the gases issuing from a salt cake pot, decomposing fourteen hundred weight of salt every four hours. The trial was continued for twenty-four hours in succession; the acid obtained varied from fifteen to twenty-two, and it averaged twenty degrees Baumé at 15° C. In England the smallest condensing space for such a quantity of salt would have been a coke tower of seven by seven by forty feet, holding about 200 cubic feet and possessing a coke surface of about

20,000 superficial feet. Compare that with my sixty cubic or fifty-eight superficial feet which did ninety per cent. of the work !

The coke tower certainly possesses one important advantage over its dwarf rival, the plate tower. The former holds a large stock of liquid, serving as a regulator for the unavoidable inequalities in the composition of the gases, whereas the latter possesses no such regulating stock. But this drawback can and ought to be counteracted by placing in front of the plate tower ten or fifteen stoneware receivers of the usual type, or a few large stone tanks, through which the acid condensed in the plate tower gradually flows onward, and issues from the last of the receivers at full strength ; the gases are made to travel the opposite way, *viz.*, first through the receivers, and then through the plate tower. In this case the stock of acid contained in the receivers serves the same purpose as that contained in a coke tower.

Most of the 130 plate columns hitherto sold, serve for another purpose than those I have so far mentioned, *viz.*, for the recovery of nitric acid from the lower oxides of nitrogen by means of contact with air and water. I believe there is a general agreement on the point that no other existing arrangement for that purpose comes up to mine. In 1889, when the Jury of the International Exhibition at Paris listened to an explanation of the new methods for producing chlorine, based on the use of nitric acid, it was taken for granted on all sides that the problem of recovering nitric acid from nitrous fumes had been definitely solved by my apparatus. As far as the manufacture of commercial nitric acid is concerned, it is significant that both the rival inventors of new condensing systems for that acid, Mr. Guttman and the Griesheim Company, much as they differ in every other way, employ the plate column at the end of their plant, for dealing with the nitrous vapors. In the just-mentioned case only a few per cent. of the total acid pass through the column ; but in all those cases where nitric acid is employed as an oxidizing agent, and where the lower nitrogen oxides, evolved in that process, had been formerly lost, or only quite incompletely recovered, the plate column now steps in as the coping stone of the edifice. Instances of this kind are the production of chlorine in any one

of the processes doing this by the aid of nitric acid, with or without the intervention of manganese or other agents; the manufacture of arsenic acid from white arsenic, or of phthalic acid from naphthalene tetrachloride; the manufacture of iron mordant for dyeing purposes; that of blue copperas from metallic copper, and too many other cases to be enumerated here. Formerly, whenever the treatment of nitrous gases was at all attempted, this was done by a string of perhaps a hundred separate receivers, or by a coke tower, the latter being saddled with the great drawback already mentioned, *viz.*, its reducing action, in a case where the very opposite action is called for. In the March number of the *Journal of the Society of Chemical Industry*, Mr. Guttman mentions the fact that at the works managed by him a small plate tower, ten feet high, performed the work formerly done by a coke tower forty-eight feet high, but much better; for the former made acid of  $40^{\circ}$ , the coke tower only such of  $30^{\circ}$ , and the plate tower actually satisfied the requirements of the Government Inspector, concerning the complete condensation of the nitrous gases, better than any other known apparatus.

In conclusion I beg to point out one more interesting use of plate columns. When gases have to be dried, by bringing them into contact with moderately concentrated sulphuric acid, which has generally been done by coke towers, the plate column is most evidently in its proper sphere, on account of its cleanliness, its chemical resistance to any attack, and the inconsiderable height to which the acid has to be pumped.

Many other uses of the plate column will no doubt suggest themselves to the industrial chemist; but I will bring my remarks to a close, and not detain you any longer with my invention.

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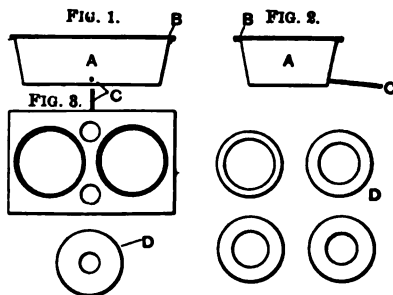
### DESIGN FOR WATER BATH.

By A. W. NIBELIUS.

THE following is a description of a water bath with constant water level, which I have found to be satisfactory in practical work:

Fig. 1 represents a longitudinal and Fig. 2 a transverse sec-

tion, and Fig. 3 a plan view of the bath. A is a common sheet iron "dripping pan" of the hardware trade,  $10 \times 6\frac{1}{4}$  inches at the top and three inches deep, transformed by enamelling into so-called agate ware. C is a brass tube  $\frac{1}{4}$  inch outside and  $\frac{1}{8}$  inch inside diameter, and  $3\frac{1}{2}$  inches long, soldered fast near the bottom of the pan and connected by a  $\frac{5}{16}$  inch rubber tube with the constant water level apparatus. The tube is inclined somewhat, so as to prevent steam bubbles remaining therein and thus interfering with the siphon action. On the pan is loosely laid a  $\frac{1}{4}$  inch thick china plate,



B, in which are two 4 and two 1 inch holes, the latter, when not in use, to be covered with china crucible covers. In the former fit five china rings (D) with holes of the following diameters: 3,  $2\frac{5}{8}$ ,  $2\frac{1}{8}$ , 2, and  $1\frac{9}{16}$  inches, into which will fit respectively No. 3, No. 2, No. 1, No. 0, and No. 00 Griffin's low wide shaped beaker glasses. On the rim of the three inch hole in the china ring a No. 4 and a No. 5 beaker can be placed, and on the rim of the four inch hole in the plate can rest a No. 6 and a No. 7 beaker. Of course, only one ring at a time can rest on the flange of the large holes in the plate.

By means of the constant water level apparatus the water in the pan is kept at a uniform depth of  $1\frac{1}{4}$  inch, and in order to keep this quantity of water constantly boiling it will be necessary to employ the flame of a kerosene oil stove having a four inch wick, or one Bunsen burner.

I have found this water bath to be clean, of reasonable price and sufficiently large for one laborant doing ordinary laboratory work.

Messrs. Eimer and Amend, of New York City, will furnish the above described water bath, they having arranged to have the china plate and rings made by the Royal China Works, of Berlin.

## CERTAIN DISTINCT ADVANCES IN THE ANALYTICAL CHEMISTRY OF RECENT YEARS.<sup>1</sup>

BY ALBERT B. PRESCOTT.

OF the important gains made by the present generation of chemists let us acknowledge (1) the resolute attempt to find out the composition of matter as a whole in any and all of its mixtures of whatever source.

Analytical workers have undertaken to resolve the complex mass and account for all its contents. It has been their ambition to identify and determine existing molecules of every sort within a given mixture, while synthetical workers have sought to reach the constitution of the molecules themselves. The task of complete analysis has been entered upon, that called "proximate" as well as that called "ultimate." There have been good investigations that have taken "extractive matter" and "empyreumatic matter" and "bituminous matter" and other undetermined residues as subjects for the beginning of chemical work rather than the end of it. The task of the complete analysis of matter in its every possible portion is a task that has been recognized and entered upon as a necessity of chemical advancement.

I do not by any means infer that the determination of distinct compounds is the result of analytical chemistry alone, as but one of the divisions of the science. On the contrary I would emphasize the dependence of the analyst upon the entire body of chemical learning. He is limited by this dependence even for the identification and estimation of distinct bodies without going into the make-up of molecules. Analysis is or ought to be a certain function of the whole body of chemistry, not a part of the body which could live if separated. An analyst can not well be less than a whole chemist, and though his ends be single in direction, they are not indifferent to the powers common to all chemical insight.

The analytic method began to yield large returns in the last century. When Black made more exact qualitative examination of fixed air he began to uncover the chain of underlying truth laid bold of by Priestley and early developed by Lavoisier and other contemporaries. In the first half of this century the

<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1900.

enormous analytical detail instituted by Berzelius extended the very foundations of physical science. And in the present generation the analyses of biological chemists and industrial chemists of many and various purposes have been very influential factors in the support of great principles of chemical truth.

Again, the courage of analytical effort in recent years has been seen especially

(2) In the elaboration of methods for the isolation of carbon compounds, both natural and artificial. "Proximate organic analysis" is not so greatly at a discount as it was twenty years ago. Research has been devoted to the estimation of organic compounds, unbroken and unaltered. It has been a common necessity to effect determinations truly "proximate," in the definition of this inadequate word. There have been pointed inquiries from the biologist often, from the metallurgist at times, from the theoretical chemist not seldom, what is the chemical character of this body as it exists just before its analysis? Since Dragendorff devised ways of plant analysis, and Hoppe-Seyler collected methods of physiological analysis, thousands of contributions have enriched the resources of the organic analyst and thousands of workers are now in like endeavor. Chemical literature is thickly strewn with directions for analysis to the end of the identification of the integral molecule, representing matter in its living state, if such a figure of speech may be used. This is indeed the special task of analytical research, although the terms of analysis are also given to operations that accompany synthetic work, to wit:

(3) In studies of the molecular structure of bodies produced by nature, bodies mineral, vegetable, and animal, as well as those of artificial production. To classify analytical work strictly by definition, which, however, I have no desire to do, all the studies of molecular constitution come within the range of analytical inquiry. But even under customary classification of chemical labor, it will be observed that certain instruments of observation early used by analytical chemists have since been found most effective in studies of molecular structure even for what is termed the configuration of the molecule. Especially, therefore,

(4) In the employment of physical methods of inspection, whereby molecular change is avoided, important advances have been made in the analyses of recent years.

First of all through the several responses of the molecule to light, under more exact observation, the clearest of identifications have been obtained. Optical methods have multiplied and become more exact. We are, however, only in the beginning of their adaptation to analysis. Studies of geometric isomerism have shown the analyst how rich in results the polarimeter may become. Next to this, probably, stands the refractometer in its value as a means of recognition in analysis. Then the use of the spectroscope for studies of absorption by transparent bodies has already done admirable service to analysis, both organic and inorganic. New responses of matter to heat have been brought under observation. In qualitative determination, as in the finding of the molecular mass, the freezing point and the effect on solidifying points of solvents are in question as well as the melting points and boiling points. The chemical world is alive with interest in the advances of the new physical chemistry. To these advances no one is and is to be more indebted than the analyst. Solubility itself, the great common factor of analytical operation, is under investigations in which the analyst has the keenest interest. The feebleness of adhesion, too often overlooked, causing waste in quantitative separations and putting limits upon the best of our results for analytical recovery, these, with the phenomena of capillarity, are well under investigation. The very checks of control analyses serve as data for studies in molecular physics.

It is not possible for me to group together in classes near all the ways of advance in recent analytical chemistry, and I will but specify once more how this advance appears.

(5) In the reciprocal benefits of scientific research and of technical skill. We see this in the work of experts: those in biological and pathological analysis, sanitary and forensic analysis, industrial and commercial analysis, agricultural and metallurgical analysis. Chemical literature during the last ten years shows how promptly discoveries like those of Emil Fischer in the sugar group, or those of Liebenberg upon the analysis of

alkaloids, those of Gladstone on refraction equivalents, or those of Baeyer upon the phthaleins, become well reduced to practice in the operations of analytical work. The simple volumetric estimations of acid and alkali are expanded in ten-fold application in thousands of analytical laboratories by means of varied indicators from the color discoveries of coal tar chemists such as Otto Witt. Analysis bows its acknowledgment of indebtedness to synthetic research. The interests of the section of analytical chemistry are all interwoven with the interests of all the sections of this congress. The analytical chemist will be a good listener to all the papers in the rich and varied repertory of the week before us.

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#### ON THE ARTIFICIAL PRODUCTION OF PETROLEUM.

BY DR. C. ENGLER.

SCIENTISTS have discussed very often in the last few years the question in which way petroleum, this source of wealth, with its special scientific interest for this country, was formed by nature. According to one theory it is generated from inorganic materials. Sokoloff thinks, that petroleum was produced during the period of the formation of our planet out of cosmical hydrocarbons, which in the beginning dissolved in the soft mass, separated from it later on. Mendeleeff assumes that water entering by fissures and chasms the interior of the earth came in contact with melting carbide of iron and produced so in a simple manner oxide of iron and the hydrocarbons of petroleum. Strong objection cannot be made to these two theories from the chemical standpoint; but the composition of the different kinds of petroleum is against them, and geology considers them not free from objections.

For a series of years the idea that petroleum was produced from the remains of plants by a kind of a distillation process, was most generally adopted, especially by chemists. Chemical and geological reasons are against this theory. From the chemical standpoint it seems quite impossible that the substance of the plants could be split up by distillation into petroleum without


<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.



leaving charcoal or coke. There would also be a genetic connection between coal and petroleum; but in occurrences of the ordinary kind, coal is nearly always absent. If this were really the case, then there ought to be with every oil occurrence in close connection a coal bank, which really seldom happens.

By a third theory the remains of animals form the raw materials from which petroleum is formed in nature. There are many facts proving the decay of masses of animals which we find now in banks in the crust of the earth in the form of the remains of shells, fishes, saurians, etc. Prominent scientists, amongst them the Americans, Wrigley, Whitney, Hunt, and others, and in Europe Höfer and Ochsenius especially, defend this idea on geological grounds. But I will not enter into the geological discussion preferring to try to give an answer to the question: How can the transmutation of animal remains into oil be imagined?

In order to answer this some thousands of salt water fishes and also shells have been distilled under strong pressure. The result was a liquid, containing mostly nitrogenous bases, such as pyridin, which was little or not at all similar to petroleum. I then recalled some experiments of Wetherill and Gregory, who found that the wax found in cadavers, the so-called "Adipocere," was nothing else but the fatty residue, which remains after the putrefaction of all the other animal matter, especially of the nitrogenous constituents of the cadaver. It is also well known that even fossil bones frequently contain fat. The question now raised was this: Could not the process in nature have been a similar one: should not first of all the nitrogenated animal substance have been destroyed leaving the fat, which was then transformed into oil. In order to prove chemically this possibility, I submitted animal fat (train-oil) to distillation—first in a sealed glass tube, later on in a large iron vessel—under a pressure of twenty-five atmospheres at a moderate heat (300–400° C.) and to my great delight found that under favorable conditions seventy per cent. of the train oil was transformed into petroleum. This equals ninety per cent. of the theoretical output. Besides the oil some water and some combustible gas was



always formed. The same behavior has been shown by other fats like butter, the fat of hogs, artificial fats, also the chemically pure glycerids of the fats like tri-olein, tri-stearin and the free fatty acids. All could be transformed into petroleum by distillation under pressure, when managed in the proper way.

This liquid, which you see here, is the distillate of the fish oil, and I have isolated from it almost all the hydrocarbons which have been discovered in the petroleum of Pennsylvania. The other products—the oil burning in this small lamp, too—are oils obtained from the crude material by purification.

But not only illuminating oils are produced. I separated also by distillation those lighter hydrocarbons which compose the gasoline, the ligroin, the benzine, etc. Recently I have succeeded in finding and separating paraffin wax and lubricating oils from those parts of the crude oil which show a high boiling point. This removes the objection of O. Ross to my theory of the formation of petroleum from animal remains. As a matter of fact I have found in the distillate obtained by decomposition of train oil, nearly all the constituents which have been separated from the natural crude petroleum, and even the gases, which, like natural gas, consist essentially of marsh gas.

Very recently I have made close investigations on the mechanism or on the chemism of the formation of the hydrocarbons of the petroleum produced by distillation of fat under pressure. This paper is published in a recent number of the *Berichte der deutschen chemischen Gesellschaft*, 1893, **26**, 1436. These experiments prove that the simpler organic acids split up in the same way, yielding almost the theoretical quantity of the respective hydrocarbon. Thus phenylacetic acid yields toluene. For further details I am obliged to refer to the paper itself. I need only remark, that we have to assume that the acids with high molecular weights are decomposed with the production of a number of hydrocarbons.

To recapitulate, it is a geological fact that we find in nature the remains of antediluvian animals as shells, fishes, saurians accumulated in masses. Whether these animals have been piled up in consequence of a natural super-production in special places in the ocean, or by currents, or in consequence of great

revolutions of the earth, this must be decided by geology; but the remains exist.

Now in which manner do the organic substances of these animals become decomposed?

The animal substance consists essentially of nitrogenated material and fat. The former is easily decomposed, the latter is very stable, a fact which has been very well known for a long time and has been shown again by exact investigations. Therefore we find the wax of cadavers in old graves, therefore the fat in the bones of mammals thousands of years old, therefore the fat on the bottom of the ocean recently found.

Whether and how far the fat was decomposed in this long period by the water splitting up glycerol and forming the free acid, for instance the fat in the bones of mammals, cannot be answered. Both, fat as well as the fatty acids form petroleum, when distilled under pressure.

We can imagine, that such remains wrapped in mud and transported by the currents in the ocean, easily accumulate and later on, under the pressure of sedimentary layers or strata, perhaps under the influence of heat too, are transformed into petroleum. This is only one of the many possibilities by which the mechanical process of the transmutation of fat into petroleum may have happened.

Under any circumstances I think I have proven that from the chemical standpoint, the formation of petroleum from animal remains has the greatest probability, as we are able now to transform every animal fat into petroleum.

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### THE DETERMINATION OF PHOSPHORIC ACID BY THE TITRATION OF THE YELLOW PRECIPITATE WITH STANDARD ALKALI.<sup>1</sup>

BY HENRY PEMBERTON, JR.

**I**N the year 1882, I described a process for determining phosphoric acid, volumetrically, by ammonium molybdate, on the principle of Wildenstein's sulphuric acid determination, or of Gay Lussac's silver method. An *aqueous* solution of am-

<sup>1</sup> Read at the stated meeting of the Chemical Section of the Franklin Institute, held September 19, 1893. Communicated by the author.

monium molybdate is run into the solution of the phosphate until no further precipitate is formed.

But it is not of this process that I now have to speak. It is referred to here, in order to draw attention to the concluding paragraph of the paper, as follows:

"I have obtained very sharp and accurate results by determining the amount of yellow precipitate (formed as above, after thorough washing), by means of a standard solution of caustic alkali, using litmus as an indicator; a description of which I hope to present in a future paper. I mention it here simply to place the fact on record." (*Journ. Frank. Inst.*, 113, 193; *Chem. News*, 46, 7.)

At that time I did a considerable amount of work upon the last-mentioned process, with very satisfactory results. A study was made of the conditions most favorable to obtaining a phosphomolybdate precipitate of constant composition, using solutions of disodium hydrogen phosphate of known strength, and also a solution of apatite, the determinations being checked by standard methods.

Before the process was in shape for publication, however, my attention was called to work of an entirely different nature, and no description of the method was published other than that embodied in the above-quoted paragraph.

Since that time several chemists have described processes based upon the same principle.

E. Thilo, in the analysis of Thomas slag (*Chem. Ztg.*, 11, 193), dissolves the yellow precipitate in standard ammonia, and titrates back with acid, using litmus as an indicator.

Franz Hundeshagen (*Ztschr. anal. Chem.*, 28, 171) uses standard sodium hydroxide in excess, and titrates back with nitric acid, using phenolphthalein as an indicator.

C. E. Manby (*J. Anal. Appl. Chem.*, 6, 82) determines the phosphorus in steel, iron, and iron ores, by dissolving the yellow precipitate in ammonia, acidifying with nitric acid, evaporating to dryness, and heating gently to expel nitric acid and ammonium nitrate. He then titrates, using the same solution and indicator as Hundeshagen employs.

James O. Handy (*J. Anal. Appl. Chem.*, 6, 204) avoids

the evaporation and heating and titrates directly as Thilo and Hundeshagen do, using standard soda and phenolphthalein. M. Rothberg and W. A. Auchinvole (*J. Anal. Appl. Chem.*, **6**, 243) also describe the same process.

Although it is now eleven years since I drew attention to this process, its advantages are so great that any information touching it, in addition to that furnished by the foregoing chemists, may be of interest. It far surpasses in quickness the process described by me (on the Gay Lussac or Wildenstein principle) and at the same time lacks nothing in accuracy. In most of the papers of the above-mentioned chemists, the process is applied to the determination of phosphorus in small quantities, as it occurs, for instance, in iron, steel, or ores. During the past year, I have had occasion to apply it to the examination of a number of phosphate rocks, as well as of strong solutions of phosphoric acid, containing over fifty per cent.  $P_2O_5$ , and the method has been used continuously during that time. I am indebted to Mr. Edwin Harris, who had charge of most of the laboratory work of the factory, for many of the figures given below. It was seldom that two tests of the same material differed more than 0.1 per cent. in  $P_2O_5$ , even when the total  $P_2O_5$  present amounted to as much as forty per cent. to fifty per cent. of the substance analyzed.

The following solutions are used:

*Ammonium Molybdate*.—Ninety grams of the crystals are dissolved (in a large beaker) in somewhat less than one liter of water. This is allowed to settle, over night, and the clear liquor decanted into a liter flask. The small quantity of insoluble molybdic acid, always present, is dissolved in a little ammonia and added to the main solution. Should the molybdate be found to contain traces of  $P_2O_5$ , a few decigrams of magnesium sulphate are added, ammonia being added to faint alkalinity. The whole is then made up to one liter. It is this *aqueous* solution that is used, *no nitric acid whatever being employed*. Each cc. precipitates three milligrams of  $P_2O_5$ .

The *ammonium nitrate* solution is simply a saturated aqueous solution of the salt. Distilled water is poured into the bottle of crystals in quantity insufficient to dissolve them all. Even in

cold weather, ten cc. of this solution is amply sufficient for each test.

The *nitric acid*, used for acidifying the solution of the phosphate, has a specific gravity of 1.4 or thereabouts.

The *standard potassium hydroxide* solution is of such strength that one cc. = one mgm.  $P_2O_5$ . One hundred cc. of it will neutralize 32.65 cc. of normal acid. It can be made from normal potassium hydroxide (that has been freed from all carbonate by barium hydroxide), by diluting 326.5 cc. to one liter. But its strength is best determined empirically by a direct test upon a phosphate solution of known strength, precipitating with ammonium molybdate and making the analysis as described below, all potassium carbonate having first been removed by barium hydroxide.

The *standard acid* has the same strength, volume for volume, as the potassium hydroxide and can be made by diluting 326.5 cc. of normal acid to one liter. In testing it against the alkali, phenolphthalein (and methyl orange) should be used.

The *indicator* can be either litmus, rosolic acid, or phenolphthalein. I have used the latter almost exclusively, as it has been shown, by J. H. Long (*Am. Chem. J.*, 11, 84) that titrations with this indicator in the presence of ammonium salts are perfectly reliable if the amount of the ammonium salt present is not excessive, if the solution is cold, and if the phenolphthalein is used in sufficient quantity. One gram of the phenolphthalein is, accordingly, dissolved in 100 cc. of sixty per cent. alcohol, and at least 0.5 cc. of this solution is used for each titration. The washing of the ammonium phospho-molybdate is done by water. (Isbert and Stutzer, *Ztschr. anal. Chem.*, 26, 584.) It may be of interest to quote from their results, since it is by some chemists thought necessary to wash with a neutral or acid solution of an ammonium salt. In all tests, as made by them, twenty-five cc. of the sodium phosphate solution were precipitated by ammonium molybdate and the phosphoric acid determined therefrom, as magnesium pyrophosphate in the usual manner.

When the yellow precipitate was washed with ammonium nitrate solution, there were obtained :

- (1)..... 0.1943 gram  $P_2O_5$  in 50 cc.
- (2)..... 0.1948 gram  $P_2O_5$  in 50 cc.

When washed with water, there was found:

- (3)..... 0.1947 gram  $P_2O_5$  in 50 cc.  
 (4)..... 0.1942 gram  $P_2O_5$  in 50 cc.

In order to establish the fact more certainly, the precipitate was washed with unusually large quantities of water:

	cc. of water used in washing.	$P_2O_5$ found.
(5).....	300	0.1947 in 50 cc.
(6).....	400	0.1944 in 50 cc.
(7).....	500	0.1948 in 50 cc.
(8).....	1,000	0.1940 in 50 cc.

There is, accordingly, no danger of loss in washing the yellow precipitate with water.

The following is the method of performing the analysis:

One gram of the phosphate is dissolved in nitric acid, an excess of which can be used with impunity, and the solution filtered into a 250 cc. flask and made up to the mark. The solution can even be poured into the flask without filtering, since the presence of a little insoluble matter does not interfere in the least with the titration. Moreover, since most phosphate rocks seldom contain over ten per cent. of insoluble matter, and as this has the sp. gr. of at least 2, it occupies a volume of about 0.05 cc., an amount so small that it may be neglected. (For instance, even in the case of a phosphate rock containing forty per cent.  $P_2O_5$ , the error is only 0.008 per cent.  $P_2O_5$ .)

After the clear solution has been poured off, it is well to treat the sand, etc., at the bottom of the beaker, with a cc. or so of hydrochloric acid, in the warmth, to insure complete solution.

It is not necessary to evaporate to dryness. Isbert and Stutzer have shown, in their paper, that when the yellow precipitate is washed with water, the soluble silica is removed, and that evaporation (to render the silica insoluble) is superfluous. Their results are corroborated by the test analysis that will be given below. In the event of its being desirable to remove silica by evaporation, for any purpose, the evaporation should be performed over a water bath, or, if on an iron plate, with great care, since, otherwise, meta or pyro phosphates are formed with results that are correspondingly low.

Twenty-five cc. of the solution (equal to 0.1 gram) are now

taken for analysis. It may be thought, by some, that an analysis made upon so small a quantity of material as one decigram, and with a standard solution representing only one milligram per cc., may be liable to errors that would not exist, when using larger quantities or stronger solutions. But it should be borne in mind that the accuracy of measurement with a twenty-five cc. pipette, is precisely the same, whether ten grams of the original substance are taken or only one gram. Any error in measuring with a pipette is, of course, entirely independent of the quantity in solution. In regard to the amount of material to be manipulated (filtered, washed, etc.) it will be remembered that the weight of the yellow precipitate is over twenty-eight times the weight of the  $P_2O_5$  contained in it. Every milligram of  $P_2O_5$  is accordingly represented by more than twenty-eight milligrams of precipitate. The standard alkali, although representing only 0.001 gram per cc. is in reality more than three times as strong as the decinormal solution generally employed. Of course, in the case of materials containing only ten to fifteen per cent.  $P_2O_5$ , as in fertilizers, two or three grams can be taken for analysis, if desired, instead of one gram.

Returning, therefore, to the method of the analysis, twenty-five cc. of the solution are measured out and delivered into a beaker holding not more than 100 to 125 cc. A large beaker requires unnecessary washing to remove the free acid in washing the yellow precipitate. The solution is neutralized with ammonia—until a precipitate just begins to form—and five cc. of nitric acid of sp. gr. 1.4 added. Ten cc. of the ammonium nitrate solution are added, and the entire bulk of the solution made up to fifty to seventy-five cc. by adding water.

Heat is now applied and the solution brought to a full boil. It is then removed from the lamp, no more heat being applied and treated *at once*, with five cc. of the aqueous solution of ammonium molybdate, which is run into it from a five cc. volume pipette, the solution being stirred as the precipitate is added. The beaker is now allowed to rest quietly for about one minute, during which time the precipitate settles almost completely. The five cc. pipette is filled with the molybdate solution, and a part of its contents allowed to drop in, holding the beaker up



to the light. If a formation of a yellow cloud takes place, it is at once perceptible, in which case the remainder of the pipette full is run in, the solution stirred and allowed to settle. A third pipette full is now added as before. Should it cause no further cloud, only about one-half of its contents is added, the remainder being run into the beaker into which the filtrate and washings from the yellow precipitate are to go. In the test analyses given below, it will be shown that even when *fifteen cc. in excess* of the molybdate, were purposely used, over and above the calculated amount, the results were accurate—no molybdic acid coming down with the yellow precipitate.

It is seldom that more than fifteen cc. in all (three five cc. pipettes full) of the molybdate have to be added. Since each cc. precipitates three milligrams  $P_2O_5$ , fifteen cc. will precipitate forty-five milligrams  $P_2O_5$ . This is equivalent to forty-five per cent. on the 0.1 gram taken for analysis, and it is not often that any material to be examined contains over this percentage. In the analysis of materials rich in phosphoric acid, it is one of the embarrassing features of the usual process, in which the *nitric acid solution* of the molybdate is used, that, in the first place, large quantities of the precipitant have to be used (frequently several hundred cc.), and, in the second place, that the analyst is never certain that enough has been added to throw down all of the phosphoric acid. This necessitates frequent testings of small portions of the phosphate solution, or of the filtrate. There is another difficulty peculiar to the process as usually carried out in all methods in which the determination is made directly upon the phospho-molybdate itself, in that much care must be observed to keep the solution at a certain temperature, since otherwise molybdic acid contaminates the precipitate and the analysis is rendered worthless. In the process herein described, using an *aqueous* solution of the molybdate, the point at which sufficient of the precipitant has been added is easily seen. No molybdic acid separates, because, in the first place, no great excess of molybdate is added; and because, in the second place, the solution is filtered immediately, or as soon as it has settled, which requires only a minute or two. The time required from the first addition of the molybdate to the beginning of the filtra-

tion is never over ten minutes, and is generally less. The filtrate and washings from the precipitate when treated with additional molybdate solution, give, on standing on a hot plate for an hour or so, a snow-white precipitate of molybdic acid, showing that all of the phosphoric acid has been precipitated. I have observed this hundreds of times.

A slight correction should be made to the statement made above in regard to fifteen cc. of the molybdate precipitating forty-five milligrams of  $P_2O_5$ . This is not strictly true, for the reason that a small quantity (something over one cc.) of the molybdate is required to neutralize the solvent action of the nitric acid. Therefore, in *very* high grade phosphates a fourth five cc. pipette full may be required.

The yellow precipitate is now filtered through a filter seven centimeters in diameter, decanting the clear solution only. This is repeated three or four times, washing down the sides of the beaker, stirring up the precipitate, and washing the filter and sides of the funnel above the filter each time. The precipitate is then transferred to the filter and washed there. When the precipitate is large it cannot be churned up by the wash water and cannot be washed down to the apex of the filter. This is generally the case when there is over ten or fifteen per cent. phosphoric acid present in the substance analyzed. In such an event, I am accustomed to wash the precipitate back into the beaker, and to fill the funnel with water above the level of the filter, doing this two or three times, then washing the precipitate back into the filter. It is not necessary to transfer to the filter the precipitate adhering to the sides of the beaker.

It goes without saying that during the washing no ammonia must be present in the atmosphere of the laboratory. Inasmuch as the beaker, funnel, filter, and precipitate are small, the washing does not take long to perform. It requires, in fact, from ten to fifteen minutes, even when large precipitates (= thirty to forty per cent.  $P_2O_5$ ) are handled. The precipitate and filter are now transferred together to the beaker. By pressure with the tip of the finger upon the double fold of the filter, it is easily given a sideways motion and lifted out of the funnel without any danger of breakage, the precipitate being still within it.

The alkali solution is run in until the precipitate has dissolved, at least twelve drops of the phenolphthalein (1:100) are then added, and the acid run in without delay until the pearly color disappears and the solution is colorless. The presence of the filter paper does not interfere in the least. The reaction of the indicator is not so sharp as when only acid and alkali are used, but it is easy to tell with certainty the difference caused by one drop of either acid or alkali. After deducting the volume of acid used from that of the alkali, the remainder gives the percentage of  $P_2O_5$  directly, each cc. being equal to one per cent.  $P_2O_5$ . Thus, if there are 28.3 cc. of alkali consumed, the material contains 28.3 per cent.  $P_2O_5$ , when one decigram is taken for analysis. From the time the twenty-five cc. are measured out until the result is obtained, from thirty to forty minutes are required.

I have applied this process to determinations of phosphoric acid in phosphates and fertilizers, and have had no experience in determining phosphorus in iron, steel, or iron ores. I am inclined to believe that in the presence of such large quantities of iron salts when using the *aqueous* solution of the molybdate it may be necessary to guard against contamination of the yellow precipitate by ferric hydrate, perhaps by using larger quantities of nitric acid than five cc., and perhaps by washing the precipitate at first, with dilute nitric acid. It may also be the case that the yellow precipitate will form more slowly.

The following analytical experiments were made in order to test the process.

Several sodium phosphate solutions were used at first, the strength of which was only approximately known, as the aim was to see how closely two readings would agree: equal quantities of the phosphate being taken for each pair of tests.

## A.

	cc.
(1) KHO with rosolic acid.....	15.0
(2) KHO with rosolic acid.....	15.15

## B.

	cc.
(1) KHO rosolic acid.....	30.5
(2) KHO rosolic acid.....	30.5
(3) KHO phenolphthalein.....	30.7

All titrations, after this, were made with phenolphthalein.

## C.

	cc.
(1) KHO.....	31.7
(2) KHO.....	31.8

A KHO solution was now made of such strength that one cc. = one mgm.  $P_2O_5$ .

## D.

	mgm.
(1) $P_2O_5$ .....	50.35
(2) $P_2O_5$ .....	50.55
(3) $P_2O_5$ .....	50.40

## E.

	mgm.
(1) $P_2O_5$ .....	51.6
(2) $P_2O_5$ .....	51.55

## F.

	mgm.
(1) $P_2O_5$ .....	51.05
(2) $P_2O_5$ .....	50.93

D, E, and F were solutions used in standardizing.

Two different samples of Florida phosphate rock were examined.

## I.

	Per cent.
(1) $P_2O_5$ .....	= 29.68
(2) $P_2O_5$ .....	= 29.84

## II.

(1) $P_2O_5$ .....	= 31.28
(2) $P_2O_5$ .....	= 31.34

The following were solutions of phosphoric acid:

## I.

	Per cent.
(1) $P_2O_5$ .....	= 46.78
(2) $P_2O_5$ .....	= 46.69

## II.

(1) $P_2O_5$ .....	= 44.41
(2) $P_2O_5$ .....	= 44.63

## III.

(1) $P_2O_5$ .....	= 48.95
(2) $P_2O_5$ .....	= 48.80

The effect of an excess of ammonium molybdate was tried. The soluble part of an acid phosphate was made up to a definite volume and fifty cc. taken for analysis. It was found to contain 8.28 per cent.  $P_2O_5$ . The test was repeated, using fifteen

0.2 of the hydroxide more than was used in the first trial. Result = 5.38 per cent.  $P_2O_5$ , equal to a difference of 0.08 per cent.

The following tests show that it is not necessary to remove silicic acid by evaporating to dryness before precipitating with the ammonium hydroxide.

A sample of Florida phosphate rock contained:

	Per cent
1. $P_2O_5$ when removed.....	51.21
2. $P_2O_5$ when not removed.....	51.21

Another sample of the same rock was like this:

When removed.	Per cent
1. $P_2O_5$ .....	51.5
2. $P_2O_5$ .....	51.7

Average  $P_2O_5$ ..... = 51.6

When not removed.	Per cent
1. $P_2O_5$ .....	51.5
2. $P_2O_5$ .....	51.7

Average  $P_2O_5$ ..... = 51.6

These results show that it is not necessary to remove silicic acid before precipitating with ammonium hydroxide.

The following table shows the results of the determination of phosphoric acid in the above samples of Florida phosphate rock. The results are given in per cent of  $P_2O_5$  and in per cent of phosphoric acid. The results are given for the two samples of rock, and for the two methods of determining phosphoric acid. The results are given for the two methods of determining phosphoric acid, and for the two methods of determining phosphoric acid. The results are given for the two methods of determining phosphoric acid, and for the two methods of determining phosphoric acid.

Sample	Method	$P_2O_5$ per cent	Phosphoric acid per cent
1	1	51.21	25.60
1	2	51.21	25.60
2	1	51.5	25.75
2	2	51.7	25.85
Average		51.6	25.7

Therefore, ten grams of the solution contain 0.10497 gram  $P_2O_5$ .

Weighed portions of the same solution were now precipitated with molybdate and the precipitate titrated with alkali. The results are given in Table II, the last column of which gives the number of cc. of alkali equivalent to ten grams of the solution. The indicator was phenolphthalein:

TABLE II.

	Weight of $Na_2HPO_4$ solution. Grams.	Number of cc. of KHO sol. required.	= Number of cc. KHO sol. required for 10 grams solution.
I.....	7.4975	79.05	= 105.4
II.....	7.8255	82.40	= 105.3
Average.....			= 105.35

It follows, therefore, that 105.35 cc. alkali = 0.10497 gram  $P_2O_5$ ; therefore,

$$(1) 100 \text{ cc. alkali} = 99.64 \text{ milligrams } P_2O_5.$$

The HCl solution was now titrated against the alkali, using phenolphthalein as the indicator. 99.00 cc. alkali were found to equal 99.05 cc. acid.

The HCl was then standardized against pure sodium carbonate.

(With methyl orange, cold:)

$$(a) 1.1291 \text{ grams } Na_2CO_3 = 65.45 \text{ cc. HCl}$$

(With phenolphthalein, boiling:)

$$(b) 1.1934 \text{ grams } Na_2CO_3 = 69.2 \text{ cc. HCl}$$

Therefore, 100 cc. =

$$(a) 1725. \text{ milligrams } Na_2CO_3$$

$$(b) 1725. \text{ milligrams } Na_2CO_3$$

Since 99.00 alkali = 99.05 acid, it follows that:

$$(2) 100 \text{ cc. alkali} = 1726 \text{ milligrams } Na_2CO_3$$

It has already been shown by (1) that 100 cc. alkali = 99.64 milligrams  $P_2O_5$ . Therefore, combining (1) and (2) we obtain 99.64 milligrams  $P_2O_5$  = 1726. milligrams  $Na_2CO_3$ .

Dividing each by its molecular weight, we have:

$$\text{for } P_2O_5 \dots\dots\dots \frac{99.64}{142.06} = 0.7014$$

$$\text{for } Na_2CO_3 \dots\dots\dots \frac{1726}{106.1} = 16.27$$

$$\text{Therefore } P_2O_5 : Na_2CO_3 = 0.7014 : 16.27 = 1 : 23.2.$$

In other words, 23.2 molecules of  $\text{Na}_2\text{CO}_3$  are required to neutralize the yellow precipitate containing one molecule  $\text{P}_2\text{O}_5$ .

The above figures are based upon the following atomic weights:

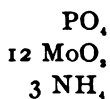
Mg .....	= 24.3
O .....	= 16
P .....	= 31.03
Na .....	= 23.05
C .....	= 12

$$\text{Mg, P}_2\text{O}_5 = 63.80 \text{ per cent. P}_2\text{O}_5.$$

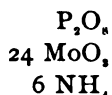
There is some uncertainty as to the correct atomic weight of magnesium. If  $\text{Mg} = 24$  (instead of 24.3 as taken above) with  $\text{Mg, P}_2\text{O}_5 = 63.98$  per cent.  $\text{P}_2\text{O}_5$ , the ratio of  $\text{Na}_2\text{CO}_3$  to  $\text{P}_2\text{O}_5 = 23.1$  to 1 (instead of 23.2 to 1). It is difficult to obtain absolutely pure  $\text{Na}_2\text{CO}_3$ ; any impurity in it will make the ratio of  $\text{Na}_2\text{CO}_3$  to  $\text{P}_2\text{O}_5$  too high.

Practically, therefore, twenty-three molecules of  $\text{Na}_2\text{CO}_3$  are required for one molecule  $\text{P}_2\text{O}_5$ . This agrees with Hundeshagen's results.

I have never seen any explanation as to why twenty-three molecules of alkali are required to neutralize one molecule of the ammonium phospho-molybdate. A discussion of the subject, therefore, may be of interest. Hundeshagen has shown (*loc. cit.*) that (neglecting any water of crystallization) the yellow precipitate, after thorough washing with water, has the following composition:

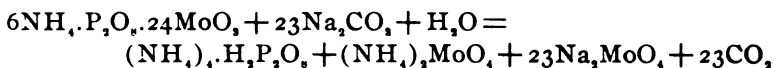


Or, doubling the formula, for the sake of clearness:



R. T. Thomson has shown in his researches on indicators (*Chem. News*, 47, 127) that of the three hydrogen atoms in  $\text{H}_3\text{PO}_4$ , two must be saturated with alkali before the reaction with phenolphthalein will be neutral, the next drop of alkali after this causing the red color to appear. Writing the formula

differently,  $H_3P_2O_7$  must become  $R_4H_3P_2O_7$  (R being the radical  $NH_4$ , or any alkali metal). Therefore, when the yellow precipitate is broken up by alkali, only four of the six molecules of  $NH_4$  are required to form (with the  $P_2O_7$  of the precipitate) a phosphate of ammonium that is neutral to the indicator. The remaining two molecules of  $NH_4$  unite with one molecule of  $MoO_3$ , yielding also a salt that is of neutral reaction. This leaves twenty-three molecules of  $MoO_3$ , representing the "net available acidity" (if I may use the expression) of the ammonium phosphomolybdate. These twenty-three molecules of  $MoO_3$ , of course, require twenty-three molecules of  $Na_2CO_3$  (or its equivalent of  $KHO$ ) to form  $Na_2MoO_4$ . Q. E. D. The following is the formula representing the reaction:



It may be well to give a short résumé of this method. One gram of phosphate rock, or two or three grams of fertilizer are dissolved in nitric acid, and without evaporating to dryness diluted to 250 cc. The solution need not be filtered. Twenty-five cc. of the solution are delivered into a four-ounce beaker and neutralized with ammonia—until a precipitate just begins to form—and then treated with five cc. of  $HNO_3$  of 1.4 specific gravity. Ten cc. of a saturated solution of ammonium nitrate are added and the solution diluted to a volume of fifty to seventy-five cc. It is then brought to a full boil, removed from the lamp and five cc. of the *aqueous* solution of ammonium molybdate added. This is followed by a second and a third five cc., if necessary, the precipitate allowed to settle, and filtered at once through a seven centimeter diameter filter. It is washed thoroughly with water by decantation and on the filter. The filter and precipitate are transferred bodily to the beaker. Standard alkali is then run in and at least 0.5 cc. of phenolphthalein (one per cent. solution) added, and then standard acid, until the color vanishes. Each cc. of alkali equals one milligram of phosphorus pentoxide.



## IRON AND STEEL.

EDITED BY P. W. SHIMER.

A MODIFICATION of the stannous chloride method for iron titrations has been proposed by R. W. Mahon (*Am. Chem. J.*, 15, 360): If mercuric and platinic chlorides are added to a solution of ferric chloride, strongly acid with hydrochloric acid, at or near the boiling point, stannous chloride reduces all the iron first, and the first drops in excess cause the formation of a faint cloud of mercurous chloride, darkened and rendered instantly perceptible by finely divided mercury and platinum which are precipitated at the same time. A very minute trace of platinic chloride present in solution is sufficient to bring about this reaction. This mixture, then, of mercuric and platinic chlorides, is an indicator which can be used to advantage in titrations of iron by stannous chloride. The indicator can be made from solutions of platinic chloride and mercuric chloride to contain in one liter, 0.05 gram metallic platinum and 34.0 grams mercuric chloride. Fifteen cc. is a suitable quantity to be used in each estimation.

The standard solution of ferric chloride is advantageously made of such strength that one cc. contains 0.01 gram iron, the stannous chloride solution of approximately the same strength. The determination of iron in its ores is made as follows: Weigh accurately about one gram of ore into a 250 cc. beaker. Cover with a watch glass and digest in twenty cc. hydrochloric acid of 1.20 sp. gr. until decomposed. Add now 0.3 gram of potassium chlorate and digest a few minutes longer. The glass and rim of the beaker are washed down into the solution, which should now be about forty cc. in volume. It is filtered and washed into an Erlenmeyer flask; twenty to thirty cc. hydrochloric acid of 1.20 sp. gr. are added to the solution bringing its volume up to about 125 cc. Now add fifteen cc. of the indicator solution and it is ready for titration. Heat the covered solution to boiling. The trace of chlorine remaining escapes. Lower the light and titrate at incipient boiling. The burette should be of 100 cc. capacity.

The residue is prepared for titration by fusing with sodium carbonate, extracting with water and acid, and adding fifteen cc. indicator.

## THE ATOMIC WEIGHT OF MOLYBDENUM.

BY EDGAR F. SMITH AND PHILIP MAAS.

Received September 25, 1893.

THE present atomic value assigned this element is based upon the results obtained by Dumas (*Ann. Chem.*, **105**, 84, and **113**, 23), Debray (*Compt. rend.*, **66**, 734) and Lothar Meyer (*Ann. Chem.*, **169**, 365). The method pursued by Dumas consisted in the reduction of molybdenum trioxide. Debray also adopted this procedure, but in addition made several experiments upon the precipitation of the trioxide in an ammoniacal solution by silver nitrate. Lothar Meyer's value (95.9) is deduced from results obtained by Liechti and Kemp (*Ann. Chem.*, **169**, 344) in their analyses of the chlorides  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$ , and  $\text{MoCl}_6$ . The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke (A Recalculation of the Atomic Weights, Washington, 1882) expresses the opinion that the most reliable results are those obtained by the reduction of the trioxide. Of the works of Liechti and Kemp he remarks, "traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weights." Rammelsberg (*Ber. d. chem. Ges.*, **10**, 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be 96.18.

Thinking that additional light could be thrown upon the magnitude of this constant, by proceeding in a different direction, we utilized a reaction first observed by Debray (*Compt. rend.*, **46**, 1098, *Ann. Chem.*, **108**, 250), which in the hands of others (Pechard, *Compt. rend.*, **114**, 173; *Ztschr. anorgan. Chem.*, **1**, 262; Smith and Oberholtzer, *J. Am. Chem. Soc.*, **15**, 18, and *Ztschr. anorgan. Chem.*, **4**, 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilized with ease in the form of an hydroxychloride— $\text{MoO}_3 \cdot 2\text{HCl}$ . Numerous trials have demonstrated that the reaction expressed by the equation,  $\text{Na}_2\text{MoO}_4 + 4\text{HCl} = 2\text{NaCl} + \text{MoO}_3 \cdot 2\text{HCl} + \text{H}_2\text{O}$ , is

quantitative. We exposed pure anhydrous sodium molybdate (at 150–200°) to the action of hydrochloric acid gas, volatilized the molybdenum trioxide, and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We recrystallized it many times, and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates, or alkaline carbonates,—substances that might have been present. The purified salt was dried with extreme care, until no further loss in weight was observed. In this anhydrous condition, it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6.9780. The balance employed by us was of the Sartorius design.<sup>1</sup>

The weights of brass and platinum were of Westphal make and had been previously carefully adjusted for the purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved, was first conducted through a U tube half-filled with damp silver chloride, it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride, and finally through clean cotton, after which it was admitted to the combustion tube, where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150 to 200°C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilized  $\text{MoO}_3 \cdot 2\text{HCl}$  was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapor repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made, after the

<sup>1</sup> We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, University of Pennsylvania, for the privilege of using this excellent instrument.

boats had remained over night in the dry desiccators, and showed no appreciable alteration. Barometric pressure and temperature were carefully observed and all weighings reduced to the vacuum standard. Our results are as follows:

Na <sub>2</sub> MoO <sub>4</sub> in grams.	NaCl. in grams.	Atomic weight of Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078
Mean.....		96.087
Maximum.....		96.130
Minimum.....		96.031
Difference.....		0.099

In our calculations we used the following values: Na = 23.05, Cl = 35.45, and O = 16. These have been taken from a revised table of atomic weights published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96.10, the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily, and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than augment the atomic weight found. Another cause of like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result 96.08 obtained by us, approaches very closely to the true atomic magnitude of molybdenum.

## IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

BY G. DE LAIRE AND FERD. TIEMANN.

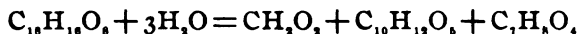
(Continued from page 355.)

*Monacetylirigenin*,  $C_{18}H_{18}O_8(COCH_3)$ .—Diacetylirigenin loses one acetyl easily if heated for a few minutes in alcoholic solution with a little soda. The monacetyl derivative forms no double compound with chloroform, but it dissolves in it readily at the ordinary temperature and may be distinguished in this way from irigenin. From chloroform monacetylirigenin separates in fine, white needles melting at  $169^\circ$ .

ANALYSIS.—CALCULATED FOR  $C_{30}H_{18}O_9$ .

	Per cent. C.	Per cent. H.
Calculated.....	59.70	4.48
Found.....	59.75	4.74

*Decomposition of Irigenin*.—By heating with concentrated alkalis irigenin is decomposed according to the equation



into formic acid,  $CH_2O_2$ , an aromatic oxy-acid,  $C_{10}H_{12}O_6$ , which we call iridinic acid and a phenol which we call iretol.

An alkaline irigenin solution is decomposed differently in presence of oxygen. The decomposition must take place, therefore, with exclusion of air. It is best effected as follows: Fifteen grams irigenin and thirty cc. water are placed in a 500 cc. pressure flask. The air is displaced by hydrogen, ninety grams of a solution of caustic potash (sp. gr. 1.33) corresponding to about thirty grams KOH added, the flask closed as quickly as possible and heated on the water bath for five to six hours. After opening the flask it is acidified at once with thirty grams sulphuric acid which has been diluted with twice the bulk of water. In a well-conducted operation no precipitate will separate from the light yellow acid solution. The formic acid may be distilled off quantitatively in a stream of water vapor; about three hours are necessary. If it is not desired to determine the formic acid, the acid solution is shaken ten to twelve times with ether. The watery residue from the evaporation of the ether is freed from formic acid by distillation in water vapor.

The air in the retort is now replaced by a stream of hydrogen and a boiling saturated solution of barium hydroxide added until the contents are alkaline. The stream of hydrogen is then exchanged for one of carbon dioxide, which precipitates the excess of barium hydroxide. The filtrate from barium carbonate is exhausted with ether. In this way the greater part of the barium iridinate separates in crystals, while the ether takes up the iretol. This is left by distilling off the ether as a syrup, which after some time sets to a mass of crystals. The iridinic acid is obtained by decomposing the barium salt with sulphuric acid and evaporating the filtrate from the barium sulphate.

We have measured the formic acid produced in this reaction. In doing this we have not forgotten that by the prolonged action of hot alkali upon iridinic acid and iretol small amounts of other volatile organic acids are formed as by products. We have determined by comparison with pure iridinic acid and iretol how far the yield of formic acid is affected, and corrected the results obtained in accordance therewith. According to the above equation 100 parts irigenin should give 13.06 per cent. formic acid, 58.9 per cent. iridinic acid, and 43.3 per cent. iretol. We have obtained from 100 parts irigenin as a mean of many determinations: 10.23 per cent. formic acid, forty to forty-five per cent. iridinic acid, and thirty-three to thirty-five per cent. iretol.

In view of the ease with which the product of this reaction decomposes and the fact that secondary decompositions even with careful working cannot be entirely avoided we may conclude with safety from the above figures that the decomposition of iridin as expressed by the above equation corresponds to the facts.

*Formic acid*,  $\text{CH}_3\text{O}$ .—The formic acid split off from irigenin is identified by its reducing action upon salts of mercury and silver. We have also converted it into ethyl formate as well as into a sodium salt. The latter when analyzed gave:

	Per cent. Na.
Calculated .....	33.83
Found.....	33.94

*Iridinic acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_6$ .—Iridinic acid is easily purified by recrystallizing from boiling benzene. It forms colorless prisms

melting at  $118^{\circ}$ , dissolves in water, alcohol, ether, chloroform, acetone and boiling benzene, is less easily dissolved by cold benzene, and is insoluble in light petroleum.

## ANALYSIS.

	Calculated for $C_{10}H_{11}O_6$ .	Found	
C .....	56.60	56.45	56.56
H .....	5.66	5.87	5.85

Heated above its melting point it splits up into carbon dioxide and a phenol which we call iridol.

Iridinic acid is a strong acid. It expels carbonic acid from the carbonates of the metals of the alkalies and alkaline earths and saturates the alkaline hydroxides molecule for molecule. Titration with caustic soda gave the following results:

For formation of  
 $C_9H_{11}O_5CO_2Na$   
is requisite.

Calculated.....	9.83 per cent. Na
Found .....	9.80 per cent. Na

The alkaline salts and the calcium salt of iridinic acid are deliquescent. The barium salt, however, crystallizes well. Its composition corresponds to the formula  $Ba(C_{10}H_{11}O_6)_2 + 5H_2O$ . The water of crystallization is lost at  $105^{\circ}$ .

## ANALYSIS.

	Per cent. $H_2O$
Calculated for $5H_2O$ .....	13.87
Found .....	13.90

A barium determination in the dried salt gave:

	Per cent. Ba.
Calculated for $Ba(C_{10}H_{11}O_6)_2$ .....	24.51
Found .....	24.58

The esters of iridinic acid are formed by passing hydrochloric acid gas through solutions of iridinic acid in the different alcohols.

*Methyl iridinate*,  $C_9H_{11}O_5(CO_2CH_3)$  is a viscous oil, boiling above  $360^{\circ}$ .

## ANALYSIS.

	Calculated for $C_{11}H_{14}O_6$ .	Found.
C .....	58.41	58.16
H .....	6.19	6.30

*Ethyl iridinate*,  $C_8H_{11}O_2(CO_2C_2H_5)$  forms a yellow oil which cannot be distilled without decomposition at the ordinary atmospheric pressure.

## ANALYSIS.

	Calculated for $C_{12}H_{16}O_6$ .	Found.
C.....	60.00	59.74
H .....	6.67	6.52

Besides the hydroxyl of the carboxyl group iridinic acid contains a second hydroxyl, whose hydrogen is easily replaced by acyls and alkyls.

*Benzoyl iridinic acid*,  $C_9H_{10}O_2(OCOC_6H_5)(CO_2H)$  is obtained by shaking an alkaline solution of iridinic acid with benzoyl chloride. The substance is precipitated from the alkaline solution by means of hydrochloric acid and recrystallized from alcohol. Its melting point is  $131^\circ$ .

## ANALYSIS.

	Calculated for $C_{17}H_{16}O_6$ .	Found.
C.....	64.56	64.58
H .....	5.07	5.24

*Acetyliridinic acid*,  $C_9H_{10}O_2(OCOCH_3)(CO_2H)$  is formed by heating iridinic acid with acetyl chloride. The excess of acetyl chloride is driven off on the water bath, the residue dissolved in benzene and precipitated with light petroleum. This compound is easily soluble in water, alcohol, ether, benzene, and chloroform, and insoluble in light petroleum, and melts at  $125^\circ$ . Alkalies separate from it acetic acid with great ease. As a control of the composition we have effected this saponification and determined by titration the acetic acid resulting from distillation with sulphuric acid.

100 parts $C_{12}H_{14}O_6$	should give	23.62 parts $C_2H_4O_2$
100 " " "	have given	24.21 " "

*Methyliridinic acid*,  $C_9H_{10}O_2(OCH_3)(CO_2H)$  crystallizes in white plates easily soluble in water, alcohol, ether, and benzene, insoluble in light petroleum, and melts at  $120^\circ$ . To prepare it iridinic acid is digested in methyl alcohol solution with sodium methylate and methyl iodide. Under these conditions the methyl ester of methyliridinic acid is formed, which by evapo-



ration of the methyl alcohol separates as an oil and is converted by saponification with alkali into methyliridinic acid.

## ANALYSIS.

	Calculated for $C_{11}H_{14}O_6$	Found.
C.....	58.41	58.22
H .....	6.15	6.15

*Silver Methyliridinate*,  $C_9H_{10}O_2(OCH_3)CO_2Ag$  is precipitated from the solution of the ammonium salt as a gelatinous mass and obtained by recrystallization from alcohol in beautiful white needles.

*Action of Hydriodic Acid upon Iridinic Acid*.—By boiling with hydriodic acid, methyl iodide is formed from iridinic acid from which it is evident that it contains methoxyl. We have applied Zeisl's method of methoxyl determination to iridinic acid and obtained the following results:

	Per cent. $OCH_3$ .
Calculated for $2(OCH_3)$ in $C_{10}H_{12}O_3$ .....	29.25
Found .....	33.13

Iridinic acid therefore contains two methoxyl groups and its formula in accordance with the experiments so far described may be written  $C_7H_4(OCH_3)_2(OH)(CO_2H)$ .

*Iridol*,  $C_8H_{12}O_3 = C_7H_4(OCH_3)_2(OH)$ .—The phenol derived from iridinic acid by splitting off carbon dioxide must have the same formula as that just obtained for the acid. Iridol is obtained by dry distillation of iridinic acid. At  $239^\circ$  a colorless oil passes over which solidifies in the receiver to large white crystals melting at  $57^\circ$ . Iridol is nearly insoluble in cold water, but is easily dissolved by alcohol, ether, ethyl acetate, benzene, chloroform, and caustic alkali. Ferric chloride colors the alcoholic solution violet.

## ANALYSIS.

	Calculated for $C_8H_{12}O_3$	Found	
Per cent. C.....	64.22	63.81	63.88
Per cent. H .....	7.14	6.98	7.05

Iridol is a true phenol and is converted on heating with chloroform and caustic alkali into two isomeric aldehydes. One, which belongs to the ortho series, is colored a deep yellow by caustic alkalies like salicylic aldehyde. The second, which is a

derivative of paroxybenzaldehyde does not give this reaction. It crystallizes in white needles which melt at 88°.

*Benzoyliridol*,  $C_6H_5(OCH_3)_2OCOC_6H_5$ , is obtained by shaking an alkaline solution of iridol with benzoyl chloride. It dissolves easily in alcohol, ether, and chloroform, as well as in ethyl acetate and crystallizes in white plates which melt at 68°.

## ANALYSIS.

	Calculated for $C_{18}H_{16}O_4$	Found.
Per cent. C.....	70.59	70.31
“ H.....	5.88	5.94

*Methyliridol*,  $C_6H_5(OCH_3)_2$ , is obtained by the action of methyl iodide upon a methyl alcohol solution of iridolsodium. It is a colorless oil, boiling at 236°–237°.

## ANALYSIS.

	Calculated for $C_{10}H_{14}O_3$	Found.
Per cent. C.....	65.95	65.62
“ H.....	7.69	7.71

By oxidation with potassium permanganate methyliridol is converted into *trimethylgallic acid*,  $C_6H_2CO_3H(OCH_3)_3$ , 3.4.5, which melts at 168°.

## ANALYSIS.

	Calculated for $C_{10}H_{12}O_6$	Found.
Per cent. C.....	56.60	56.49
“ H.....	5.66	5.78

In order to identify the trimethylgallic acid sharply, we have converted it into gallic acid on the one hand by digestion with hydriodic acid, and on the other hand we have prepared it by methylating gallic acid. Finally we have determined that by dry distillation silver trimethylgallate gives the trimethyl ether of pyrogallol, melting at 47° and boiling at 235°, and that this is converted into pyrogallol when it is heated to 150°–160° in closed tubes with dilute hydrochloric acid.

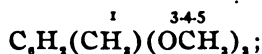
Trimethylgallic acid and the trimethyl ether of pyrogallol have been known for a long time. W. Will<sup>1</sup> prepared them by permethylating gallic acid and pyrogallol, and G. Körner<sup>2</sup> has shown that the syringic acid obtained by him from the gluco-

<sup>1</sup> Ber. d. chem. Ges., 21, 607 and 2023.

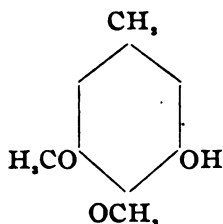
<sup>2</sup> Gazz. Chim. Ital., 18, 216.

side of the elder (dimethylgallic acid) is converted by methylating into trimethylgallic acid of melting point  $168^{\circ}$ . We have found the properties of the compound in question to be exactly those which W. Will gives it.

*Constitution of Iridol.*—Trimethylgallic acid is formed from methyliridol by the oxidation to carbonyl of a methyl group attached to the benzene nucleus. Methyliridol corresponds therefore to the formula,



it is the trimethyl ether of homopyrogallol,  $\text{C}_6\text{H}_3(\text{CH}_3)^1(\text{OH})^{3,4,5}$ . Iridol contains one hydroxyl in place of one of the three methoxyl groups of methyliridol. We have already observed that iridol is transformed by chloroform and alkali into two isomeric aldehydes. It must therefore contain two hydrogen atoms in the benzene nucleus, of which one occupies the ortho, the other the para position with reference to the phenol hydroxyl. Only the formula



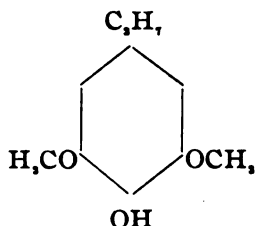
is in accordance with these facts.

There are other grounds for this view. A. W. Hofmann has isolated two phenols from the acid constituents of wood tar boiling between  $250^{\circ}$ – $290^{\circ}$ , of which one, boiling at  $265^{\circ}$ , is a dimethyl ether of homopyrogallol<sup>1</sup> while the phenol boiling at  $285^{\circ}$  bears the same relation to propylpyrogallol<sup>2</sup>. If we exchange the methyl in the methoxyl groups of these phenols for hydrogen we obtain triatomic phenols which show the characteristic reactions of pyrogallol. For this reason A. W. Hofmann considered these phenols derivatives of pyrogallol.

<sup>1</sup> *Ber. d. chem. Ges.*, 12, 1371.

<sup>2</sup> *Ber. d. chem. Ges.*, 8, 67; 11, 327.

Nitric acid converts the dimethyl ether of propylpyrogallol into the dimethyloxyated quinone<sup>1</sup>,  $C_6H_2O_4(OCH_3)_2$ , melting at  $249^\circ$ . In the first named compound the propyl and hydroxyl groups must occupy the para position with reference to each other. W. Will<sup>2</sup> has shown that the trimethyl ether of Hofmann's propylpyrogallol is converted by potassium permanganate into trimethylgallic acid melting at  $168^\circ$ . The above dimethyl ether of propylpyrogallol must therefore have the formula



It is *a priori* probable that the lower homologue of the above phenols—the dimethyl ether of homopyrogallol—has an analogous constitution. We have, in fact, determined that the neutral methyl ether of the phenol boiling at  $265^\circ$ , prepared by A. W. Hofmann, of which a large sample was at our disposal, had the same properties and the same constitution as the trimethyl ether of homopyrogallol prepared from iridol. Both compounds are converted by the aboxydation of the methyl group attached to the nucleus into trimethylgallic acid melting at  $168^\circ$ .

The dimethyl ether of pyrogallol from the wood tar and iridol are isomeric methyl derivatives of the same homopyrogallol. The properties of the two isomers differ materially as the following summary shows:

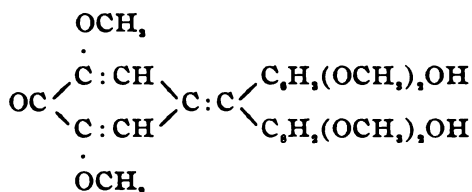
	Dimethyl ether of homopyrogallol from wood tar.	Iridol.
Melts at .....	$36^\circ$	$57^\circ$
Boils at .....	$265^\circ$	$239^\circ$
Benzoyl derivative melts at.....	$118^\circ$	$68^\circ$

By means of a very remarkable method which is analogous

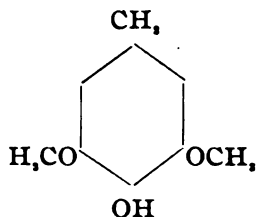
<sup>1</sup> A. W. Hofmann. *Ber. d. chem. Ges.*, 11, 332.

<sup>2</sup> *Ber. d. chem. Ges.*, 21, 2025.

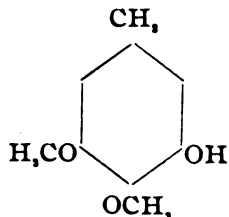
to the formation of rosanilin by the oxidation of a mixture of toluidin and anilin, namely, fusion with sodium hydroxide in contact with air, the mixture of the dimethyl ether of homopyrogallol boiling at  $265^{\circ}$  and of the dimethyl ether of pyrogallol is converted as A. W. Hofmann has shown<sup>1</sup> into eupittonic acid,  $C_{22}H_{16}O_8$ , the constitution of which, in view of the studies made in the last few years of the triphenylmethane colors should be expressed by the symbol:



To such a condensation, however, only a dimethyl ether of homopyrogallol constituted according to the formula



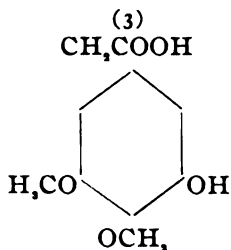
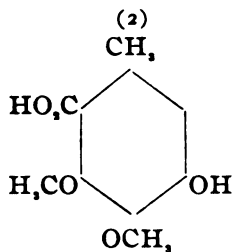
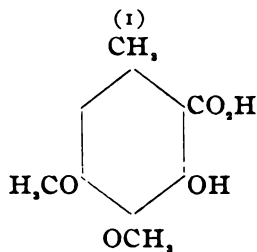
can lend itself. Its isomer, iridol, which under like conditions gives no trace of eupittonic acid or an isomeric eupittonic acid must therefore have the formula,



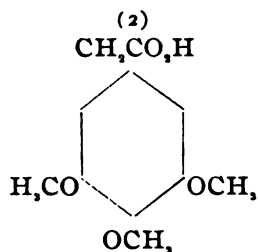
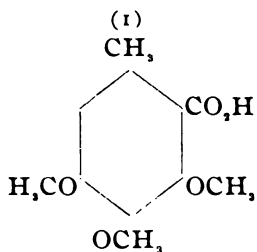
This gives to iridol the same constitution as our experiments.

<sup>1</sup> *Ber. d. chem. Ges.*, 12, 1377.

*Constitution of Iridinic Acid and Methyliridinic Acid.*—Iridinic acid is carboxylated iridol and its composition must correspond to one of the three formulas



while the constitution of methyliridinic acid is expressed by one of the two formulas



The experiments described below give the further explanation of the constitution of iridinic and methyliridinic acids.

(a) *Dibrommethyliridinic Acid*,  $C_6Br_2(OCH_3)_2(CH_2CO_2H)$ .—If a solution of methyliridinic acid in dilute acetic acid is poured into an excess of bromine water an acid separates in compact crystals which is easily soluble in alcohol and ether. It melts

at 152° and is formed from methyliridinic acid by the substitution of two bromine for two hydrogen atoms.

## ANALYSIS.

	Calculated for $C_{11}H_{13}Br_2O_3$	Found.
Per cent. Br .....	41.66	41.36

The formation of this acid shows at once that of the two formulas considered for methyliridinic acid the second is correct.

(b) *Dibromtrimethylgallic Acid*.—Dibrommethyliridinic acid is a very stable compound which may be recrystallized from hot dilute nitric acid without change. If it is heated with nitric acid of sp. gr. 1.2, action takes place accompanied by the evolution of red vapors and soon leads to a profound decomposition of the dimethyliridinic acid used. If, however, the action is stopped at the proper time by the addition of water, which can be determined by the precipitation of crystals instead of an oil, and the solid compound separating dissolved in very dilute nitric acid, dibromtrimethylgallic acid will crystallize out in long lustrous needles which when pure melt at 143°. For comparison we have prepared dibromtrimethylgallic acid by pouring a solution of trimethylgallic acid in dilute acetic acid into excess of bromine water, and find the acid obtained in these different ways to be identical.

## ANALYSIS.

	Calculated for $C_{10}H_{10}Br_2O_4$	Found.
Per cent. Br .....	43.24	43.54

Experiment shows that methyliridinic acid contains two hydrogen atoms directly attached to the benzene nucleus. We have not been able to convert dibrommethyliridinic acid into dibrommethylgallic acid by heating it with potassium permanganate. The potassium permanganate is indeed reduced by heating for a long time and a small part of the dibrommethyliridinic acid destroyed; but by far the larger part of the acid remains unattacked.

(c) *Trimethylgallic Acid from Methyliridinic Acid*.—Methyliridinic acid is, on the contrary, readily oxidized to trimethylgallic acid, melting at 168°, by means of potassium permanga-

nate. In carefully conducted oxidations in the course of the transformation an extremely unstable intermediate product, which is difficult to isolate and which is probably the ketonic acid derived from methyliridinic acid,  $C_6H_5(OCH_3)_2COCO_2H$ , and which we have not followed further.

(To be continued.)

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## ON CARBORUNDUM.

(CARBIDE OF SILICON.)

BY DR. OTTO MÜHLHAUSEN.

THIS new material stands next to diamond, not only in its composition, but in its internal and external properties, in the extraordinary brilliancy of its crystals, and in the extreme hardness which makes it such an efficient and powerful abrasive material.

It is an American invention, having been discovered by Edward G. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles.

The product is obtained by heating a mixture of 100 parts sand, twenty-five parts salt and twenty-five parts coke in an electrical furnace for several hours. The alternating current used has finally a strength of about 500 amperes and a difference of potential of fifty volts.

The mixture yields a mass in which we can distinguish shells and layers of different character and nature. Around the carbon core we find a layer of graphite. The latter is surrounded by a thick shell of carborundum crystals. This shell of carborundum is enveloped in a thin sheet of amorphous carbide of silicon; surrounding and incasing these three products of the reaction is the original mixture in an essentially unchanged condition.

(1) *The Graphite*.—The graphite is located around the carbon core and is covered by the carborundum crystals. It is connected with the latter, forming one large elyipsoid of crystals whose rays are arranged radially to the axis of the elyipsoid or

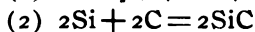
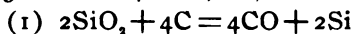


core. The inner part of this shell contains the black graphite crystals, the outer the carborundum.

Those parts next to the core consist of pure carbon, and possess all of the properties of graphite—blackening the fingers with metallic luster, feels soft, unctuous, etc. These graphite crystals occur in hexagonal flakes and resemble, sometimes, iodine crystals. Their form is that of the carborundum, out of which they are produced. As wood after being charred still keeps its structure, so carbide of silicon keeps its form when transformed by heat into graphite. The silicon is simply eliminated,  $\text{SiC} = \text{C} + \text{Si}$ , and a skeleton of the original structure is preserved in carbon.

(2) *The Carborundum Crystals.*—The carborundum crystals occur as the chief products of the reaction between carbon and silicon. They are located between the graphite and a layer of what seems to be an amorphous form of carbide of silicon. The whole mass of the crystals forms a green shell which is easily crushed and separated into the individual crystals. Their color is greenish gray, greenish yellow, greenish blue, etc. Their size differs very much, and depends upon the quantity of material brought into action, on the operation itself, and on the time of the reaction. The crystals are often so small that their shape can only be recognized with the microscope; often so large that they have a diameter of several millimeters.

We must assume that the process takes place according to the equation,  $\text{SiO}_2 + 3\text{C} = 2\text{CO} + \text{CSi}$ ; or,



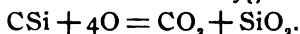
These crude crystals consist essentially of carbide of silicon, besides some impurities—oxide of aluminum, iron, etc. In order to clean the crystals, to free them from the impurities attached to them, a sample of the crude material as it came from the furnace was crushed, pulverized, floated, and finally prepared in the form of a very fine powder. This was placed in a combustion tube, heated to a red heat, and treated with a current of oxygen. Being thus burnt in oxygen, it was boiled alternately with caustic soda, water, hydrochloric acid, and afterwards it was given a prolonged treatment with hydrofluoric

acid to which a little sulphuric acid had been added. This action being over, all silicon tetrafluoride, hydrofluoric and sulphuric acids were driven off, and the powder washed and dried.

By this treatment carbide of silicon was obtained in an almost pure state.

The pure silicon carbide has a specific gravity of 3.22. It is insoluble in all of the ordinary solvents, as hydrochloric, nitric, sulphuric, and hydrofluoric acids, but it is decomposed by caustic and carbonated alkalies.

Heated to a white heat in a platinum crucible, the powder shows a yellow green golden color of remarkable beauty, some of the powder being at the same time burnt up. The loss per hour is about one-half per cent. This indicates that silicon carbide is very little combustible in oxygen:



It is easy to decompose it by heating with substances like chromate of lead or oxide of iron, and with a mixture of chromate of lead and bichromate of potash it even explodes.

The very fine powder, when floated in water, does not entirely settle, even after several months; this property of suspension is, however, immediately ended by adding acids or salts.

(3) *The Amorphous Carbide of Silicon.*—This substance forms a layer of greenish gray, bluish green, and white particles of the size of the original sand from which they evidently originate. The particles have no definite form, are very soft and therefore easily crushed to a fine powder, and this was found to contain the same constituents as the carborundum. It was evident that it was an amorphous form of carbide of silicon and therefore a somewhat similar process of purification was employed.

The cleaned powder consists essentially of silicon carbide in an amorphous form. Its specific gravity is 3.22, the same as the crystallized variety. It seems, however, to be more easily combustible.

(4) *The Unaltered Mass.*—The next material we come to is a mass of the original mixture, which has been very little, or not at all, changed by the operation of the furnace.

(5) *The Gases*.—The gases evolved at the beginning, during, and near the ending of the reaction have been analyzed. They consisted of a mixture of hydrocarbons derived from fresh coke and oxide of carbon with a small admixture of air.

Samples are not shown because you probably have already seen the display of this splendid material in the gallery of the mining building. This new material seems to me likely to cause a revolution in the abrasive market.

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### RAPID METHOD FOR THE DETERMINATION OF MANGANESE IN MANGANESE BRONZE.

By JESSE JONES.

Received September 21, 1893.

THE following method is in use in this laboratory for the determination of manganese in manganese bronze. It is an adaptation of a well-known method in common use for the determination of manganese in iron and steel. A determination can be made in less than one hour, and as the amount of manganese in the ordinary run of work seldom exceeds 0.10 per cent., the method gives fairly satisfactory results.

*The Method*.—Dissolve five to ten grams of drillings in nitric acid of 1.20 sp. gr., using a large beaker to avoid frothing over. An excess of acid must be avoided as it interferes with the precipitation of the copper by hydrogen sulphide. When solution is complete, transfer to a 500 cc. cylinder without filtering out the precipitated stannic oxide. Make up to 300 cc. and pass a rapid current of hydrogen sulphide from a Kipp's apparatus until the supernatant liquid is colorless. Decant off through a dry filter, 180 cc. corresponding to three or six grams of sample, and boil down rapidly to about ten cc. Transfer to a small beaker and add twenty-five cc. of strong nitric acid. Boil down one-half, make up with strong nitric acid, boil, and add one spoon full of potassium chlorate. Boil ten minutes and add another spoon full of potassium chlorate. Boil till free from chlorine, cool in water, and filter on asbestos, using filter pump. Wash with strong nitric acid through which a stream of air has been passed. When free from iron wash with cold water until no acid



remains. Place the felt and precipitate in the same beaker and dissolve in ferrous sulphate, using five cc. at a time. Titrate back with permanganate until a pink color remains. Deduct the number of cc. used in titrating back, from the number of equivalents of ferrous sulphate used and the remainder shows the manganese in the amount of sample taken.

*Permanganate Solution.*—Dissolve 1.149 grams potassium permanganate in 1,000 cc. water; one cc. equals one mgm. manganese. Check by dissolving 0.1425 grams ferrous-ammonium sulphate in a little water and acidulating with hydrochloric acid. This should precipitate ten mgms. of manganese. If not, apply the factor of correction.

*Ferrous Sulphate Solution.*—A solution of ferrous sulphate in two per cent. sulphuric acid, so dilute that five cc. corresponds to ten cc. permanganate solution. This is best made by trial and dilution.

CHEMICAL LABORATORY,  
WM. CRAMP & SONS, PHILADELPHIA.

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, etc.*—501,022, July 4, McCoy, J. H., ore concentrator. 500,662, July 4, Lockhart, W. S., ore separator. 500,604-605-606, July 4, Payne, C. Q., magnetic ore separator. 501,879, July 18, Fitzgerald, J. J., ore separator and amalgamator. 501,999, July 25, Fraser, A., ore crushing machine. 501,494, July 18, Davis, O. W., Jr., ore roasting kiln. 500,582, July 4, Jones, J. M., ore pulverizer. 501,188, July 11, Iles, M. W., flooring for blast furnaces. 500,621, July 4, Sheedy, D., and M. W. Iles, apparatus for separating matte from slag. 502,167, July 25, Bates, F. G., metallurgical furnace. 500,684, July 4, Westerman, F., regenerative coke oven. 501,107, July 11, Siemens, F., regenerative gas furnace and producer. 502,181, July 25, Fauvel, C. J., refractory ores, treatment of; incandescent particles of freshly roasted ores are struck as they descend by crossing jets of water, while the air is excluded. 501,996, July 25, Emmens, S. H., electrolytic bath. 501,997, July 25, Emmens, S. H., electrolytic separation of metals. 501,783, July 18, Hermite, E., electrolysis of saline solutions, using a thin layer of mercury to form amalgam of metal with base.

*Iron and Steel.*—501,200, July 11, Wailes, J. W., open-hearth steel melting furnace. 501,138-139-140, July 11, Heath, J., and Holden, G. H., apparatus for manufacture of iron and steel. 500,979, July 4, Tweedy, E., apparatus for hardening steel.

(5) *The Gases*.—The gases evolved at the beginning, during, and near the ending of the reaction have been analyzed. They consisted of a mixture of hydrocarbons derived from fresh coke and oxide of carbon with a small admixture of air.

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18, Laffont, M., artificial stone, "plastic refractory argil and fusible calcined argil." 502,023, July 25, Turner, J. W., artificial stone, Portland cement, rock-lime, plaster of Paris, marble dust, and sand. 502,096, 502,097, July 25, Heller, T. J., plaster compound, sodium silicate, sodium carbonate, alum, sugar, senegal gum, salt cake, and ground china ware.

*Oils and Varnishes.*—501,988, July 25, Carman, F. J., refining sulphurous petroleum; passing vapors through a mass of melted metal, which will reduce the sulphur and combine with it. 501,227, July 11, Hojer, T. G., preservative drier, hydrated manganese dioxide, slaked lime, and a lime salt. 501,578, July 18, Pfaune, H., varnish; made by electrolyzing linseed oil which has been acidulated with dilute sulphuric acid.

*Bleaching and Dyeing.*—500,917, July 4, Lifschütz, I., violet red dye from dinitro-anthraquinone. 501,500, July 18, Gano, Leo, bluish black tetrazo compound of paradiamines. 501,118, July 11, Ulrich, M., and Lauch, R., blue black tetrazo. 501,434, July 11, Müller, C., violet, sulphuretted derivative of ortho-alkyl-oxy-para-rosaniline. 501,104, July 11, Runkel, F., greenish blue triphenylmethane dye. 501,069, July 11, Hassencamp, H., violet triphenylmethane dye. 500,761-762, July 4, Green, A. G., and Lawson, T. A., red azo dyes. 500,558, July 4, Bracewell, John, printing anilin black. 501,156, July 11, Ostersetzer, O., printing cotton fabrics. 501,160, July 11, Fitzinger, W., dyeing black.

*Oxygen from Air.*—500,697, July 4, Webb, G., Jr., composition for; made by dissolving caustic soda in hot water, heating to 100° C., adding manganese oxide and sodium manganate, evaporating to dryness, heating, cooling and breaking.

*Miscellaneous.*—500,549, July 4, Baekeland, L. H., antiseptic compound; contains sodium and potassium fluoride and common salt. 501,471, July 11, Shaw, C. H., sulphur candle. 501,036, July 4, Allen, D., soft soap ingredients; hard soap, sodium carbonate, phosphate, and chlorate, concentrated lye and water. 501,934, July 4, Nirdlinger, M., artificial fuel; bituminous coal, anthracite coal, silicate of soda, dilute sulphuric acid, coal tar and coal tar pitch, manganese dioxide, and potassium chlorate. 501,323, July 11, Bryant, W. E., insecticide, for stored grain; sulphur, slaked lime, sodium sulphite, potassium nitrate, sassafras bark, gum, camphor, and thymol. 501,235, July 11, Seifert, B. R., creosote composition; derivative from creosote and carbon dioxide. 501,845, July 18, Pohle, J. G., stove polish; plumbago, phosphoric acid and a hygrometric substance. 501,254, July 11, Pohle, J. G., stove polish; plumbago and phosphoric acid. 502,163, July 25, Apple, C. S., adhesive pencil; dextrin, cold water, glue, zinc white and glucose are used. 501,222, July 11, Dame, Paul C., artificial whale bone, made from animal hair; put first in softening bath, then in a bath of acetic acid, and then pressure is employed. 501,311-312, July 11, Albertson, and Briggs, N. B., coloring and burnishing compound; soap, wax, shellac, borax, dextrin, glue, water, coloring matter, and chromic acid are used.

*Lead.*—501,377, July 11, Smith, A. J., white lead; charge is put in corroding chambers with acid vapors and basic cream of varying degrees of concentration. 500,580, July 4, Iles, M. W., flue dust from lead smelting furnaces is charged into fusion furnaces; fused quickly; fumes are collected in screens and fusions are run out and allowed to cool.

*Zinc.*—501,189, July 11, Lewis, G. T., alkali is added to sulphide ores and roasted to produce zinc oxide. 501,559, July 18, Chanute, A., metals from compound ores containing zinc; ores are mixed with salt, roasted, fumes collected in screens, and leached with dilute hydrochloric acid, and gold and silver are separated by adding zinc to solution.

*Aluminum.*—501,553, July 18, Whitney, C. F., alloy, aluminum, 76 per cent. or more, manganese and tungsten, 12 per cent. each or less. 501,233, July 11, Richards, J. W., and Hunt, A. E., alloy, aluminum, iron and manganese (30 per cent.) with a low per cent. of carbon.

*Nitric Acid.*—500,786, July 4, Volz, C. O., the charge is placed in retort and distilled in vacuo.

*Ammonia and Cyanides.*—500,650-651, July 4, Fogarty, T. B., apparatus for manufacture.

*Ammonium Nitrate.*—500,914, July 4, Landin, J., alcohol is percolated through a solution of sodium nitrate and ammonium sulphate, and the alcoholic solution is passed through ammonium sulphate.

*Chlorine, or Caustic Alkali.*—501,121, July 11, Waite, C. N., electrolytic method, brine being first treated to form insoluble sulphates.

*Quinin, etc.*—501,066, July 11, Grimaux, E., manufacture of halogen derivatives such as chlor-hydro-sulphate. 500,665, July 4, Marckwald, W., manufacture of piperazin. 501,446, July 11, Schaal, E., manufacture of resin acid esters.

*Tanning, etc.*—501,586, July 18, Claxton, J. W., tanning hides; composition for, red oak bark, white oak bark, "h bark, salt, lye soap, soda, gum gambria, alum, and sodium phosphate. 501,797, July 18, Lussigny, H. A. A., carrotting furs; caustic alkali is used. 501,798, ditto; carbon and nitric acid are employed.

*Sugar.*—502,014-015, July 25, Prangey, L. E. A., process of refining. 501,878, July 18, Engel, G., ditto.

*Distillation of Mash.*—502,079, July 25, Ilges, R., process of separating fusel oil.

*Water.*—501,784, July 18, Herscher, C., sterilization of drinking water. 501,732, July 18, Roeske, H., purifying water by adding stratum of iron, which is agitated and subjected to electric current, filtering and aerating the water after treatment. 502,252, July 25, Hanna, D., purifying water for steam boilers.

*Earthenware.*—500,585, July 4, Klieber, J., liquid material for manufacture—clay and aqueous solution of sodium carbonate or bicarbonate.

*Plasters and Cement.*—501,937, July 25, Hawes, E. E., cement, tar, rosin, glue, vinegar, salt, flour, and sal soda. 501,794, 501,888-889, July

18, Laffont, M., artificial stone, "plastic refractory argil and fusible calcined argil." 502,023, July 25, Turner, J. W., artificial stone, Portland cement, rock-lime, plaster of Paris, marble dust, and sand. 502,096, 502,097, July 25, Heller, T. J., plaster compound, sodium silicate, sodium carbonate, alum, sugar, senegal gum, salt cake, and ground china ware.

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## NEW BOOKS.

A LABORATORY MANUAL, CONTAINING DIRECTIONS FOR A COURSE OF EXPERIMENTS IN ORGANIC CHEMISTRY. SYSTEMATICALLY ARRANGED TO ACCOMPANY REMSEN'S ORGANIC CHEMISTRY. BY W. R. ORNDORFF, A. B., PH.D., ASSISTANT PROFESSOR OF CHEMISTRY IN CORNELL UNIVERSITY. D. C. Heath & Co. 12mo.

This book, printed on one side of the paper only, to leave room for notes evidently, contains directions for eighty-two experiments, beginning with "Fractional Distillation" and ending with "Alizarin." The apparatus used is as simple as the nature of the work will allow and the questions asked or indicated by means of an interrogation mark seem to be judicious. The directions bear evidence of having been tried carefully in practice. The absolute necessity for this would seem to be self-evident, but I venture to say that in very many books of the kind it has nevertheless not been done—so much the worse for the unlucky student who repeatedly endeavors to do the impossible because his authority is good. It cannot be too strongly insisted upon that such books ought either to be put together conscientiously or not at all.

E. H.

THE PHARMACOPEIA OF THE UNITED STATES OF AMERICA. SEVENTH DECENNIAL REVISION (1890). Official from January 1, 1894. Published by the Committee of Revision. Philadelphia: J. B. Lippincott Company. Agents, P. Blakiston, Son & Co. 1893.

The Pharmacopœia of the United States has become a book of considerable dimensions—602 pages.

The metric system has been employed throughout the volume, the solids by weight and the liquids by measure. Of the coal tar antipyretics, acetanilid is the only one admitted, because the others are either made by a patented process or their names have a proprietary right. Among the articles added to the Pharmacopœia I notice peroxide of hydrogen, convallaria, cocaine, hyoscyne, sparteine, strontium bromide, and pepsin (1:3000). The terminal "e" is retained for chlorine, cocaine, bromide, *et altera*. Instead of writing chloride of sodium, or nitrate of silver, the committee make it sodium chloride, silver nitrate, and so on, putting the base first. In the case of the salts of iron and mercury this change involved the use of the respective

terms in "ous," and "ic" (ferrous and ferric, mercurous, mercuric); but as a matter of precaution they have retained "corrosive," "mild," "yellow," and "red" in the title of the respective mercury compounds; thus, "corrosive mercuric chloride," "mild mercurous chloride." Instead of the word, "official," "official" is now used.

The present Pharmacopœia contains 994 articles, ninety of those previously official having been dropped, while eighty-eight new ones have been introduced. Commercial ether and commercial chloroform have been dismissed. Arsenium becomes arsenum; aluminium becomes aluminum; creasotum is now creosotum. The work throughout is gotten up with good taste, well printed on good paper. The accuracy of the work is guaranteed by the high standing of the committee of revision.

ISAAC OTT.

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#### NOTES.

*Immunity Against Disease.*—The following appears on the editorial page of the *American Druggist* for October 12, under the caption "Germ Nuclein," and as it contains matter of general interest to chemists it is reprinted here entire.

Recent investigations of Dr. Victor C. Vaughan, of the University of Michigan, into the principles of immunity and cure in the infectious diseases, as illustrated in his presidential address to the Section on General Medicine of the Pan-American Medical Congress, mark so remarkable a step in the progress of modern bacteriology as to compel most willing admiration for the man and his work. The artificial production of immunity from disease dates back to 1796 when Jenner first made known his discovery with reference to the prevention of smallpox by inoculations of a mild form of the infection. Since then the subject of immunity against disease has received most careful consideration from many of the most brilliant thinkers in the scientific world, until it is now regarded as a special subject of scientific study, while at the same time finding place in the schools of medicine as one of the special branches of study in that science. Pasteur, the eminent French chemist, has particularly distinguished himself in this field, and his labors have won for him with other honors that of election to membership in the French Academy. His success in the treatment of rabies by inoculating the patient with sterilized cultures of the pathogenic germ, has made his name known in all parts of the civilized world, though scientists are not yet prepared to

admit that the treatment is either entirely curative or preventative. With regard to Pasteur's success in the prevention of chicken cholera and anthrax by the introduction into the tissues of modified forms of the specific germs of these diseases, it should be known that his teachings on the subject are accepted as authoritative in all schools of bacteriology.

Immunity against disease may be either artificial or acquired; and the induction of artificial immunity, according to Vaughan, may be brought about either by an attack of the disease ending in recovery; by direct inoculation with the germs of disease, according to certain recognized methods providing for either (1) vaccination with a modified or less virulent form of the infection; or (2) the introduction of at first a very small number of the virulent germs and successive inoculations with larger numbers; or by one or more treatments with sterilized cultures of the germs.

In studying the production of immunity from infectious diseases by the method of treatment with sterilized cultures, the question naturally presented itself to Dr. Vaughan as to what constituent of the culture conferred immunity, and it is from the study of this question that he has built up his theory regarding the rôle of the germ-nuclein. He has gone over the ground traversed by a number of German investigators, and, to quote his own words, he is "ready to believe that the immunizing substance is a constituent of the bacterial cell itself;" and is, besides, a poison which is capable of acting as an antidote to the greater poison of infection when administered in small doses with the latter purpose in view.

Dr. Vaughan has not limited his investigations to this either, but has proceeded further and succeeded after much experimentation in isolating active nucleins from various cellular bodies. The preparation, chemical reaction, germicidal properties and physiologic effect of these nucleins are described in detail in his address to the Pan-American Medical Congress which is printed in part in the October 7 number of that excellent medical journal, the *Philadelphia Medical News*.

The new field of study opened up by Dr. Vaughan will doubtless be fruitful of research not less in the domain of chemistry than of medicine, though practical applications of the study in its bacteriological aspect may not ensue for some years to come. Many persons who read for the first time of Dr. Vaughan's researches into the germicidal properties of the nucleins obtained from glandular organs like the testicles, thymus and thyroid will find a corroboration of the claims made in very recent times as to the therapeutic value of certain organic extracts, but further study will convince all such that the germ-nuclein theory is founded upon a more scientific basis and bears no more relation to the former than does the medication of the present day with that of ancient times.

# THE JOURNAL

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# AMERICAN CHEMICAL SOCIETY.

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## ON CHEMICAL ENERGY.<sup>1</sup>

BY DR. W. OSTWALD, OF THE UNIVERSITY OF LEIPZIG.

**D**URING the scientific development of chemistry, the hypotheses which have served as a primary foundation have always been borrowed from a prominent sister science. At the time of the most rapid development of mechanics as founded by Galileo and advanced by his pupils and successors, chemistry was mechanical; the solvent action of acids upon metals was explained by assuming that the former possessed points and edges by means of which they disintegrated the latter; bodies which combine were supposed to have hooks by means of which they attached themselves to each other. When Newton based his theory of astronomical movements upon the assumption of a force acting inversely as the square of the distance, chemistry shortly appropriated this idea, and traced all processes to the attraction and repulsion of particles. It is, therefore, not surprising that the phenomena of the Voltaic pile (which later proved to be so intimately connected with chemical changes) were at once utilized to serve as a foundation for a theory of chemical processes. These theories, especially that of Berzelius, have prevailed a long time, but finally have proved themselves just as insufficient to represent chemical phenomena as the mechanical and the attraction theory.

Thus the theory of chemical combinations is to-day a strange

<sup>1</sup>Read before the World's Congress of Chemists Aug. 26, 1893.

and contradictory conglomerate of the fossil constituents of the earlier theories. The rudiments of the theory of attractions still play the most important role, while there is also considerable discussion about positive and negative elements, *i. e.*, the residues of the electro-chemical theory, and in most recent times we see the long-forgotten mechanical conceptions again stepping to the front in stereo-chemistry and being accepted by many as a new step in the progress of science.

In such times it is of great value on the one hand to recall the historical development and the evanescence of theories; on the other hand to find in the older theories that which is useful and correct, so as to obtain sound building material for a new theory.

Especially are we forced to conclude from the fate of past theories, that chemical phenomena must be explained by their own interrelations, that is, must be logically arranged. The use of analogies from other fields of natural science has indeed often led to suppositions which for the moment seemed satisfactory; on trial, however, such analogies have always proved themselves more a drawback than a help, since they hindered the unbiased comprehension of facts, and they could not (or will not in the future) be cast aside without a great struggle and considerable sacrifice of time and labor.

It is scarcely needful, at present, to prove that the several provinces of quantitative science possess in a single conception both the principle which distinguishes them and that common principle which unites them, namely, the conception of energy. Mechanical energy is distinct from thermal; similarly, chemical energy is distinct from electrical; and in each province progress can only be made by studying the various properties which the form of energy under examination possesses.

At the same time, however, the laws which determine the correlation and conservation of energy constitute the only bond which unites the various fields. If heat could not be changed into mechanical energy, and chemical into electrical, these provinces would stand distinct and isolated from each other; and neither thermodynamics nor electro-chemistry would be possible. This shows that progress in the scientific conception of chemical phenomena depends upon primarily determining the

several properties of chemical energy as such, and then its relation to other forms of energy; this done, we will be able to cope in a scientific manner with each chemical process, no matter whether it leads to other chemical changes or causes the appearance or destruction of other forms of energy.

The knowledge of the laws of chemical energy is not only scientifically but also practically of the greatest interest. All energy which is employed in accomplishing the various purposes of industry is derived from chemical sources, the combustion of fuel. Besides each step that we take, every word that we speak, in fact every thought formulated by our brain, leads to sources of chemical energy; animals and plants throughout their whole existence are based primarily upon chemical energy and its laws, and the ultimate problems of biology are in every respect chemical.

All forms of energy have this in common, that they may be resolved into two factors, both of which have definite properties. The one, which we call intensity, determines whether the energy may remain at rest, or must undergo an exchange. Thus, for instance, the factor of intensity for heat is temperature, since we know that two bodies can be at rest with reference to their heat only when their temperatures are equal. The second factor we call capacity; it determines how much energy at a given intensity is present in the object under consideration. With heat, for instance, this is called heat capacity.

What now are the factors of chemical energy? If we had a measure for its factor of intensity, as the thermometer is a measure of the intensity of heat, we would be able to determine for each substance with reference to another whether it could react with the latter or not, just as the thermometer shows us whether or no heat can be transmitted from one body to another. Our answer is that this question has not been completely solved, but that for many phenomena we already possess a chemometer, as we might call the instrument—in analogy to the thermometer.

In order, however, to be able to explain the theory of the chemometer, the factors of chemical energy must first be more precisely determined. The factor of capacity is in this case most easily discovered. The chemical energy which is present under given circumstances is proportional to the weight or mass

of the substances involved. Hence we sell and buy chemical energy according to weight. This becomes more clear from the following consideration: When we buy coal, we do not consider the carbon present, but rather the chemical energy, since in the use of the fuel we allow the carbon to escape quietly through the chimney as carbon dioxide, without making any effort to retain it; that, however, which we husband with the greatest care, is the chemical energy of the coal, obtained as heat. I have stated with due consideration that the factor of capacity of chemical energy is proportional to the mass; yet it is not mass, since this conception belongs solely to mechanics. It is therefore by no means more correct to say "atomic mass" instead of "atomic weight," since in this case the degree of chemical capacity is concerned which is proportional to both weight and mass, without being one or the other.

The term "degree of intensity" of chemical energy has something in common with the conception which has become familiar in the field of chemistry under the term of "chemical affinity," more to denote that field in which a more accurate knowledge was especially desirable than to combine by such a word sufficiently definite ideas. The word was there, just as the name of a future street stands on a signboard in the outskirts of a city, in a waste field; tents and barracks of the most curious kind have been erected from time to time only to be deserted again; only in most recent times solid buildings and permanent settlements have found a place on this site, and soon a new section of the city will be created there, whose importance threatens to throw the older portions of the city in the shade.

J. Willard Gibbs called the degree of intensity of chemical energy the chemical potential; analogous to the degree of intensity of electrical energy, which is called the electrical potential. So, to avoid the vagueness of the term *affinity*, we will make use of the term chemical potential, or in brief potential.

Now it follows from the definition of the degree of intensity, that two substances with like potential can not act on each other; and, conversely, that when two substances act on each other, their potential must be different.

That general law which can be regarded as expressive of the

Second Theorem holds also for the chemical potential, namely: Two potentials which individually are equal to a third are equal to each other. This proposition seems quite self-evident, and therefore equally meaningless. Yet we can draw from it conclusions that are very far reaching. It says that two bodies or groups of bodies, which are in equilibrium with each other, can mutually replace each other at pleasure towards a third system in every reaction in which this third system (towards which equilibrium has been established) can react. Thus, for example, every soluble body can be replaced by its saturated solution, every liquid by its saturated vapor, every solid body at its fusing point by the melted body without causing any alteration in the equilibrium depending upon the former. Among other things, this shows that while the heat of solution, fusion, and evaporation change the evolution of heat during a chemical process they do not thus affect the equilibrium. The thermal theory of affinity, which is even to-day championed by Berthelot and others, is by this circumstance proved to be quite untenable.

It is natural, in the case of such a far-reaching proposition, to require proofs. This proof is found in the fact that it is impossible to create a perpetuum mobile. To have a perpetuum mobile it is not necessary to create energy from nothing, but only to transform potential energy into kinetic. If it were, for instance, possible to transform the constant heat which is present in enormous amounts in the ocean into work which then could change back into heat, we would require no more coal to propel our steamships, since all the work which we required for their propulsion would be transformed into heat by friction and could return to the ocean in unchanged amounts. Such a perpetuum mobile will be instantly possible when two substances which individually are in equilibrium with a third are not in equilibrium with each other. If we assume that a substance, A, when in contact with a large body, B (the ocean), assumes a temperature which is different from that imparted to a body, B, simultaneously in contact and equilibrium with the ocean, we would cause a transmission of heat between A and B which would be capable of driving a machine. This proof is equally




true for every other form of equilibrium and for every form of energy, and thus we also prove our chemical proposition.

When we have thus recognized the conditions under which energy is in equilibrium or at rest, we can directly reason that energy can not be at rest when its potentials are different. A process must then take place by means of which they become equal. This is the most common phenomenon with which we are acquainted; everything which takes place is based in the last instance upon an equalization of energies of different potentials.

Since, however, energy, as is a fact, has a never-ceasing tendency to equalize itself, the question arises why it has not done so long ago during the many thousand years which our system of worlds has existed. We continually see differences of potential existing in nature—compressed air, galvanic elements; all these contain stores of energy which are ever ready to act and must therefore be unequal. Likewise the fossil fuels and the sulphides of the metals are able in conjunction with the oxygen of the air to bring forth large amounts of energy during their interaction, and can not, therefore, be in equilibrium. Aside from the tendency for equalization, which is peculiar to energy, other forces are therefore active in nature which hinder or detain this, and an accurate understanding of these natural phenomena can only be attained when these opposing and detaining causes are known.

For mechanical and electrical energy such hindrances can be easily created. A spring may be kept wound by a weight; two electrically charged bodies, which tend to approach each other, can be kept from attaining their equilibrium by the dielectric resistance of an interposed medium. All these hindrances, however, have but this explanation, that the differences of energy present are compensated by the use of other energies, so that their equalization is prevented; at the same time, we can prove that, according to the method employed, large quantities of one form of energy of any magnitude can be compensated by equally small quantities of another form of energy, for by means of a small switch, enormous currents of electricity can be interrupted and closed at will.

In the case of chemical energy we are, however, very often



unable to prove such compensations by the application of other energies. When a piece of wood is exposed to the air, it would be in accordance with the general tendency to equalize the energy present, if combustion took place and the wood combined with the oxygen of the air. The same would apply to organized bodies. Our body consists of combustible substances; and, in accordance with the chemical affinities present, it should combine with the oxygen of the air and burn without cessation. Why is it not consumed?

If we should attempt to answer this question we should soon become entangled in inexplicable contradictions. We can not ask: "Why is our body not consumed?" since it does actually burn. It continually takes up oxygen and gives off carbon dioxide. The same answer applies to other chemical phenomena. A stick of sulphur exposed to the air seems unchanged, but it is only apparently so. In reality it is oxidized; slowly, however, and so slowly, in fact, that we would not notice it in weeks or months. If the process were, however, continued for years or decades of years, the oxidation could be measured. The rapidity of reaction is clearly proportioned to the surface. If we take finely powdered sulphur, flower or milk of sulphur, whose total surface is much greater, we can prove the formation of sulphuric acid in hours and days.


What has here been stated for a few cases is a general truth. In every case where different substances which could act upon one another are in contact without having, practically speaking, any apparent action upon each other, we can bring the requirements of the teachings of energy into unison with the actual conditions by actually ascribing to these substances an action which is, however, so slow that it lies beyond the possibilities of measurement.

We have here the means of entering upon one of the most important and mysterious problems, namely, the search after the chemical activity of organized bodies. For, as all the activity of organisms depends upon changes in their chemical energy, all knowledge in this case depends upon a correct elucidation of the character of the chemical changes. If we can understand how the chemical processes of combustion, to which all physiological sources of energy finally lead, can be so regulated that

they are able at any moment to adapt themselves to the ever-changing requirements of the organism, we have taken a step in every respect most important in the knowledge of life.

Let us take, for instance, a mixture of oxygen and hydrogen. Under ordinary circumstances we can preserve this mixture for a long time without the formation of a measurable amount of water. If, however, we place a piece of platinum sponge into it, the formation of water immediately begins; and it is as suddenly terminated when we remove the sponge. The platinum sponge has, moreover, undergone no change and is able to exert this action for an unbounded space of time.

At first, it seems as if we had here the first proposition of our later natural science; to rudely dispute "*causa arguat effectum*," since we have here a cause which can bring forth extended and large effects at pleasure without becoming exhausted. If we ask, however, what this proposition means by cause and effect we find it to be degrees of energy. No energy of any kind can be created without the consumption of an equal amount of energy, and no difference in the potential of energies can be called forth without the simultaneous disappearance of equivalent differences in the potential of other energies. The truth of these propositions is not cast in doubt by the experiment with the mixture of oxygen and hydrogen, since the heat of combustion remains the same both when combination is effected by an electric spark and when it is brought about at the ordinary temperature by means of platinum sponge. While, therefore, the law of cause, clothed in the form of a principle of energy, regulates the final result of the action in an unchangeable manner, the time during which this action takes place remains absolutely independent of this principle, and we have side by side with the absolute necessity of this law of cause the freedom with reference to the time during which it exerts its influence. Therefore we see that all possible phenomena which, originating from the same substances, reach the same products, arrive at these with a very different rapidity. The object to be arrived at is unchangeable; whether it is, however, to be accomplished in a second or in several thousand years is a circumstance over which we have full control.



The name "catalytic bodies" has been given to substances which cause chemical reactions without experiencing any change themselves. We will now change this definition so as to read thus: Catalytic substances are those which modify the rapidity of a definite chemical reaction without changing their own content of energy. To place a catalytic substance into the reacting bodies, and to remove it, requires theoretically no work. This proves that within the strict province of the law of energy, there still remains room for the greatest variation in the temporal extent of the phenomena.

This peculiar circumstance has its foundation in the fact that in the expression of most degrees of energy time is not mentioned, and that, therefore, the equation of energy does not determine the extent of time involved in the phenomena.

One exception is made in the case of kinetic energy which depends upon the rapidity. What has been stated above does not therefore apply to this form of energy. Upon what the action of catalytic substances depends is still a mystery, the solution of which is the more difficult, since it can only be explained by means of new principles, which are beyond the law of energy. At present, we must be satisfied with the knowledge that it is a fact, and must seek to become acquainted with the laws involved. A beginning has already been made; from a large number of various investigations it has been found that many chemical reactions, which usually take place very slowly, are hastened by the presence of free acids; or, to speak in the language of the modern theories, by the presence of free hydrogen-ions, and that this action is proportional to the concentration of the latter. The greatest variety of phenomena have been examined in this respect, partly by me, partly by my pupils, and I have as yet found no case where this statement did not apply. Free hydrogen-ions are therefore without doubt exceedingly active catalysators of a general character.

At the same time numberless *specific* catalysators exist which act only upon certain phenomena. These are the ferments, organized and unorganized. These also are unable to do more than to change the rapidity of certain reactions in one or the other respect, and all attempts to explain their action must be

based upon this, their sole property. The laws which they obey appear to be of an extremely complicated nature, especially with the more complex constituted ferments; this is probably due to the fact that they undergo a change themselves while influencing a certain chemical reaction.

I need not show in an extended manner that the wonderful action of living organisms can be traced to a regular impulse upon the chemical processes which take place among their constituents in accordance with general chemical laws, and that these again may be traced to the action of catalytic substances. If the rapidity of reaction in a muscle is hastened which may be regulated from a central organ, this muscle will accomplish a corresponding amount of work. When, however, the supply of energy is exhausted, the influence of a catalysator cannot force it to any further manifestations. The same is true for all other activities of organisms.

I cannot assume to have made clear the mystery of life in the previous pages, but I believe that I have solved a more apparent problem, namely, to show that the science which is seemingly abstract and foreign to actual life, and which has developed during the last years under the name of physical chemistry, is a science of the highest real importance. If it will be possible for this science to throw light upon that most difficult of all the problems of nature, the mystery of life, how much easier will it be to explain by means of the new principles the by far much easier problems of technical chemistry which have not been solved so far. It is quite natural and self-implied, but we must nevertheless repeat again and again that—"The more perfect the theoretical evolution of the sciences becomes, the greater will be the scope of their explanations and at the same time the greater their practical importance."

### THE FUNDAMENTS OF CHEMICAL THEORY.<sup>1</sup>

By J. E. TREVOR.

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*The Development of Science.*—The general course of development of the sciences which deal with natural phenomena follows,

<sup>1</sup>[This paper was delivered in the form of a lecture at Cornell University. It has been substituted by Prof. Trevor for his paper before the World's Congress of Chemists, read August 26th, entitled "The Energy Theory of Chemistry; Comment upon Ostwald's paper on Chemical Energy."—EDITOR.]

in its beginnings, through a descriptive stage. The bare facts, the materials with which a science has to deal, are laboriously collected and, in so far as is possible, they are systematically arranged. Not until this patient collection of empirical facts has gathered together a comparatively extended mass of more or less thoroughly classified material does it become possible, with this material as a basis, to begin a study of the causal relations between the different classes of phenomena coming in question. In entering upon this second stage of development the Descriptive Science becomes a Rational Science, the discovery of *facts* gives place to the discovery of *relations*, isolated phenomena appear as parts of the coherent whole, and a completed network of its exact relations makes this science a known thing, brings its phenomena under the absolute control of the all-ruling principles of mathematics. A recognition of the connection between phenomena, and not the observation and description of individual facts, is the final aim of science.


Botany, for example, is in its development just emerging from the descriptive stage. The seeking and classifying of kinds of plants has furnished a broad basis of known fact, and men seek now to know the cause of the flow of sap in trees, to follow the transformations in the growing plant and fruit, to understand the chemistry and the mechanics of plant life. The science of physics has made a considerable progress into the rational stage, its investigations are mainly conducted under the guidance of known relations between the phenomena of heat and work, of work and electricity, of electricity and magnetism, and the like. Its world of phenomena is coming more and more under the unerring control of mathematics. But the most complete, the classical instance of this advanced stage of development is offered by solar astronomy, the relations between its elements being known with such exactness that the minute details of its stupendous phenomena are foretold by computers with nothing less than an astounding accuracy. The command of man over the phenomena of the heavens is one of the most complete as well as one of the grandest achievements of the human intellect.

Our science of chemistry is in its nature like these others; its progress has hitherto been in the main that of a descriptive

science and a fearful mass of necessary chemical material has been accumulated in the course of it. And now its rapid and brilliant rationalization is attracting the attention of the scientific world.

The desultory alchemy of the middle ages had become scientific investigation when Priestley and Scheele discovered that there was such a thing as oxygen, and Lavoisier showed that matter is not to be annihilated. From this time the increase in our knowledge of descriptive chemistry has been rapid. Valuable principles of classification were furnished by the atomic hypothesis of Dalton and the molecular hypothesis of Avogadro, both appearing early in the century, and they have been employed in a systematic investigation of the properties and reactions of inorganic compounds, which has ever since been carried forward with vigor, to no slight extent under the brilliant leadership of the Swede, Berzelius. This work has been accompanied in later years by an extended study of the materials of organic chemistry, by a seeking and finding of the wonderfully simple and beautiful relations existing between the different classes of the compounds of carbon. Widespread enthusiasm and devotion in this work was kindled over a half century ago in Germany by Liebig, whose gentle memory comes down to us through the science as a charm and an inspiration. This work has enriched science with a wealth of working material, has chased back into the darkness much of the mystery of ordinary life and, in supplying the most useful of our drugs and dyes, has added greatly to the material wealth of the world.

The experimental development of descriptive chemistry, both inorganic and organic, which has made up the great bulk of chemical investigation during the present century, was necessary work and it has been rich in achievement. Yet in it and through it all there is something lacking, something which must eventually claim the supreme interest. From a descriptive science we must pass to a rational science, from the *what* of chemical phenomena we must pass to the *how* and the *why*. The observation and description of individual facts must make way for a recognition of the connection of phenomena; the primitive interest in the discovery of a new compound must vanish



to make way for a greater interest in the discovery of relations, of generalizations.

*The Rationalization of Chemistry.*—The latest phase of chemical science studies chemical processes as such, strives to rationalize chemistry, aims to make it a science of exact relations between classes of phenomena. And since chemical phenomena involve heat and electricity, density, temperature and the like, things which are specifically treated in the science of physics, the new trend of chemical work has come to be termed the physical chemistry. It is this to which we are now to turn our attention.

To say that the sciences of physics, of mechanics, and of astronomy are more highly developed, are more completely understood than are their sister sciences, is to say that they have been brought more completely under the control of mathematics. The more complete this rule over their phenomena becomes, the more perfect becomes their development as branches of human knowledge. In this respect, as the highest of them all, stands geometry. For twenty-two centuries now the geometry of Euclid has been the encouragement and guide of that scientific progress which is one thing with the advance of man from a worse to a better state; and it is even unto this day the highest aim of every scientific student to bring his science into such a state of perfection as that which has been attained by geometry. The deepest scientific insight shines through the words of the Pythagoreans, who called mathematics the Purifier of the Reasonable Soul, and it is the desire of each one of us to bring that branch of physical science in which he is more immediately interested into such a state that it too shall be, in a similar sense, a purifier of the reasonable soul.

To develop, now, a scheme which shall place chemistry upon the basis of an exact science we must clearly comprehend with *what* we are dealing, what the subject matter of our work really is. It may be conclusively shown that the actuality with which we have to do is *energy*; from a physical point of view the manifestations of energy constitute phenomena. From the laws of energy is derivable a coherent system of natural science, made up entirely of exact relations between the various energy phenomena coming in question. This enables us to construct a



wide-reaching and coherent theory of the changes of state, a chemical theory characterized by the stately march and all the relentless rigor of a strictly mathematical science.

And in this matter we must stand for conservatism. We must not countenance the wild hypotheses which have so often disfigured chemistry. Facts are the things with which we must deal, and we must deal with them rigorously. Hypotheses are to be used with the utmost caution and discarded whenever possible. In so doing we shall find that our science will become a purer one and that we shall be far less likely to fetter and blind ourselves by *belief* in hypotheses, which in themselves may be attractive but which are essentially unprovable and therefore unworthy of belief.

*Energy.*—Experience has made clear that heat, work, electricity and the like are mutually convertible; they are hence the same kind of thing and this kind of thing has received the general name Energy. Besides space and time<sup>1</sup> this is our most general conception, for these three quantities are the only ones which are common to all branches of physical science.

It has been more or less clearly understood ever since the time of Berkeley, ever since 1710, that the world which we perceive *is* our perceptions, is not something *inferred* from our perceptions. But the only things of which we can take direct cognizance are the manifestations of energy. We cannot see material objects directly with our eyes, what we actually do see is a picture upon the retina, produced by the radiant energy entering the eye—and in all probability the impression upon the optic nerves is more immediately due to the energy of the chemical changes taking place in the retina; the eye is an organ for radiant energy. The ear, likewise, reacts upon the mechanical energy of a vibrating gas, and the organs of touch react upon those forms of mechanical energy involving pressure or force as a factor. The only thing, then, of which we can take *direct cognizance* is energy, in one form or another. Energy, furthermore, despite its transformations, never increases nor decreases in amount; for example, it is impossible to create work out of noth-

<sup>1</sup> It may even be maintained that time is a derived conception, but it is difficult to see how we might dispense with it as an independent variable in treating natural phenomena.

ing and thus construct a machine which shall furnish power forever; and in any transformation of energy none is ever lost. This fact, which is based upon the widest experience of exact science, is expressed by saying that the various energy forms are mutually convertible, or, better, that the total energy of the accessible universe is constant. That which *subsists* is in its very nature a *substance*, and so, when we bear in mind that energy is the only thing of which we can directly know, we are forced to the most important conclusion that:

Energy is the only *substance* of which we *know*.

Briefly the argument is this:—

That which we perceive *is* our perceptions;

These perceptions are manifestations of energy;

Hence: That which we perceive is energy manifestations, the only thing of which we directly know is energy. Furthermore energy subsists, and is hence the only substance of which we know.

We can have no knowledge of an objective reality of matter, whether the term corresponds to anything actual we do not know and ought not to care. The notion of objective reality is inferred from the evidence of our senses; it is a derived idea, an hypothesis. The only thing of which we really know is energy, which is therefore the prime subject of human interest.

This result establishes the fundamental character of the energy idea. Any natural process is a change of one or more energy forms; the transformations of energy constitute phenomena; science, the study of phenomena, is concerned with energy alone, and its laws furnish the basis of physical theory. The rational theory of phenomena, in chemistry as well as elsewhere, is an energy theory, and its fundamental principle is the great generalization:

#### **The Energy of the Universe is Constant.**

This principle is known as the First Law of Energetics.

*Energetics.*—The different sciences would be wholly distinct were the several energy forms which they treat not mutually convertible. This convertibility, and this alone, unites them into a general Science of Energetics. By using space, energy and time as the units common to them all there are obtained throughout measurable relations between them. The subjects

of chemistry, electricity, heat, and work are thus brought together, and the respective transformations of the energies involved furnish the subject matter for the sciences of electro-chemistry, thermo-chemistry, electro-dynamics, thermo-dynamics, and mechanics.

It is especially to be emphasized that the different energy forms are of wholly independent character, no one of them is energy *par excellence*. There is no reason for assigning to the energy of motion an especially prominent character. Neither electricity nor heat is to be treated as kinetic energy, any more than kinetic energy is to be considered as electricity. And, furthermore, no energy form may be singled out as a "potential energy." The energy of distance is no less an energy than is that of motion into which it is transformable, and each energy is "potential" with respect to every other, in that it may be transformed into that other.

*The Factors of Energy.*—The possibility of developing a comprehensive and exhaustive science of Energetics depends upon the fact that the analytical expression for each energy form is resolvable into a product of two factors<sup>1</sup>, one of which has the character of an intensity of the energy form in question, and the other that of a capacity for it. They are best known as the intensity and capacity factors. The intensity factor determines whether its energy may or may not be at rest, having, by definition, the same value for two energy quantities which do not influence each other. Such is, *e. g.*, the temperature factor of heat energy; a large mass of iron and a small one may contain very different amounts of heat but no conduction will take place from one to the other if their temperatures be the same. Examples of this resolution into factors are:

	Capacity.	Intensity.	Formula.
Mechanical Energies.	Distance energy = distance	× force	$s \cdot f$
	Surface energy = surface	× tension	$O \cdot \gamma$
	Volume energy = volume	× pressure	$v \cdot p$
	Motion energy = mass	× velocity square	$\frac{1}{2} m \cdot V^2$
(Other Energies.	Electricity	= quantity × potential	$e \cdot \pi$
	Heat	$= (\frac{Q}{T})$ or $\frac{dQ}{dT}$ × temperature	$\frac{Q}{T} \cdot T$
	Magnetism	= mag. quan. × mag. potential	$e \cdot \Pi$

<sup>1</sup> Helmholtz, 1887; also J. W. Gibbs, 1876.

The recognition of the impossibility of an unlimited transformation of one energy form into another without intensity differences, as in obtaining work from a quantity of heat of uniform temperature, or from electricity of uniform potential, constitutes the so-called Second Law of Energetics:

**Unlimited conversion of an energy, without intensity differences, is impossible.**

This principle<sup>1</sup> is as entirely a result of experience as is the first law of energetics, formulating the observed impossibility of creating energy from nothing. They are the most fundamental laws governing natural phenomena; taken together they constitute the farthest reach of science.

*Energy Equilibria.*—The condition for the equilibrium of a single energy form, that its intensity shall be uniform throughout, is in its application very familiar. The heat in a bar of iron which is hot at one end will be transferred by conduction until the temperature differences shall have become equalized; a mass of gas must have uniform pressure throughout (the effect of gravitational energy supposed eliminated); electricity will not pass from one electrically charged body to another when both quantities of electricity have the same potential; two moving masses will not influence each other's motion if their velocities be the same (they must correspondingly have the same direction of motion, for the definition of a velocity includes a direction). The same rule applies to the other energy forms.

But that feature of the energy theory which is of the most especial interest at the present time is its treatment of the equilibria between several energy forms which oppose one another in the same system. Such an equilibrium is said to obtain when no transformation of one energy form into another takes place. The equilibrium eventually reached may be disturbed by a change of the intensity factor of any one of the energies involved, this causing an opposed change of the correlative energy forms. At equilibrium an infinitesimal change (virtual change) of one of the energies must be exactly balanced by the resulting virtual changes of the others.

<sup>1</sup> Generalized by Ostwald, 1892.

For the sake of illustration let us consider a billiard ball suspended by an elastic cord. When the system comes to rest an equilibrium is maintained between the gravitational energy, tending to pull the ball downward, and the elastic energy of the cord, tending to pull it upward. In a virtual displacement of this equilibrium, *e. g.*, pulling the ball an infinitely small distance downward, the gravitational energy expended is exactly equal to the elastic energy gained; their *algebraic* sum is zero. This is required by the first energy law. Suppose, however, the ball to be drawn downward a foot or two and then released. In its new position the two energies are not in equilibrium and, in the initial infinitesimal displacement as the ball rises, the expenditure of elastic energy exceeds the corresponding gain of gravitational energy. Only when the oscillations have ceased do the virtual changes balance each other.

The necessary and sufficient *condition of equilibrium* then, for any material system whatsoever, is

*The algebraic sum of the energy changes involved in a virtual displacement of the equilibrium must equal zero.*<sup>1</sup>

If we represent energy, capacity and intensity by E, C, and I respectively, this condition is expressed analytically by

$$\sum \delta E = 0 \text{ or } \sum C \delta I = 0,$$

the summation being taken over all the correlated energies of the system. It is known as the Principle of Virtual Energies and it represents the theory of all equilibria whatever, whether they be those of statics, of thermodynamics, of chemistry, or of any other branch of general Energetics.

A special case of this is the Principle of Virtual Work in statics, where the equilibria studied are between mechanical energies capable of doing work, W. When the work furnished by one in a virtual displacement is exactly counterbalanced by that of the others the mechanical system in question is in equilibrium, and the condition of equilibrium is

$$\sum \delta W = 0,$$

the same equation as before. Upon this relation, introduced in-

<sup>1</sup> Ostwald, 1892.

to mechanics by Bernouilli and Lagrange, the science of statics is based.

*Force*.—It may be well to insist at this point upon the distinction between force and work or energy, a distinction not always kept clear in popular speech. Reference to the table of energies already given will show that a *force* is an intensity and must move a body through a *distance* in order to do *work* upon it; the work done is the product of force and distance. The force meant acts in the direction in which the body moves; if a force  $f$  have a different direction the *acting force* is its component lying in the direction of motion, or  $f \cos \theta$  when  $\theta$  is the angle made by the direction of the force with the direction of motion. Opposing forces may prevent motion in which case the force is balanced and does no work. The intensity factors of the space energies, force, surface tension, and pressure, are the quotients of an energy by a distance, a surface, and a volume respectively, and they are the intensities acting through a distance, a surface, and a volume respectively. They are the same kind of quantity as is a temperature or an electrical potential. *Power* is often used as synonymous with *work*, but *force* can never be.

The term *work* is sometimes used to designate in general the energy forms which are convertible without limit, and *force* to designate their intensity factors, but in the interest of a clear terminology this usage would better be dropped.

*Units*.—In dealing with energy quantities it is necessary to have an established unit. The one generally accepted as a basis of reference is the *erg*, the unit of work. It is the product of unit force into unit distance, the product into one centimeter of the force giving to one gram of mass an acceleration of one centimeter per second in a second:

$$\begin{array}{ccccc} \text{Energy.} & & \text{Force.} & & \text{Distance.} \\ \text{Erg} & = & \text{g} \cdot \frac{\text{cm}}{\text{sec}} \cdot \frac{1}{\text{sec}} & \times & \frac{\text{cm}}{1} \end{array}$$

This erg is then  $\text{g} \cdot \left(\frac{\text{cm}}{\text{sec}}\right)^2$ , or  $mv^2$ , which is *twice* the motion energy (kinetic energy) contained in unit mass moving at unit velocity.

Nearly all the other energy units in common use are reached by the following proportionality factors:

The unit of electrical energy, of electricity, has been arbitrarily set equivalent to ten million ergs; *i. e.*

$$\text{volt-coulomb} = \frac{1}{10,000,000} \times \text{ergs.} \quad (1)$$

The gram-centimeter, being the product into one centimeter of the gram of weight, the force giving to a gram of mass an acceleration of 980 centimeters per second in a second ( $980 \frac{\text{cm}}{\text{sec}} \cdot \frac{1}{\text{sec}}$ ), is 980 times greater than the erg. So

$$\text{ergs} = 980 \times \text{gram-centimeters.} \quad (2)$$

Careful determination of the proportionality factor converting work into heat units, the mechanical equivalent of heat, has given

$$\text{gram-centimeters} = 42,750 \text{ calories.} \quad (3)$$

*Outline of Chemical Theory.*—The energy theory may be applied most interestingly in organizing into a concrete whole the exact relations of a rational chemical theory. A comprehensive treatment of the problems of the subject includes in the first place the immediate applications of the conservation law. Further than this, the energy equilibria with which the science of chemistry is concerned may be treated, for the purposes of classification, under three heads: First, those represented by differential equations, which are integrable because a known relation exists between the factors of the energy involved (as is the case with volume energy); second, non-integrable differential equations, furnishing a relation between the respective intensity factors; and, third, differential equations involving, in addition to the opposed energies of reacting substances, the influence of extraneous energy forms. These three grand divisions of the subject are then:

- I. Volume energy integrals,
- II. Simple differential equations,
- III. Reaction equilibria,

and the three corresponding types of equilibrium equation are:

$$\int dW = \int C \cdot dI \quad (1)$$

$$C' \cdot dI' = C \cdot dI \quad (2)$$

$$\Sigma C' \cdot dI' = C \cdot dI \quad (3)$$

where W, C, and I represent, respectively, work and the capacity

and intensity factors of energy forms. The general form of the equations remains  $\sum \delta E = 0$ ; in equation (3) the summation is taken over the reacting substances on the one hand and the reaction products on the other, the energy of the one decreasing and that of the other increasing in a virtual displacement of the equilibrium of a reversible reaction. The consideration, in a general way, of the results to which these equations lead will furnish at once a complete outline of our system of Chemical Theory. It will be well to glance over the outline before taking up the work in detail, in order to gain an idea of the coherence of the theory.

I. There may be calculated<sup>1</sup>, by means of equation (1), the amount of work gained in the expansion of a dissolved substance or of a gas from a given pressure  $P$  to a lesser one  $p$ . This will be

$$\begin{aligned}\int dW &= - \int_P^P v dP \\ &= -RT \int_P^P \frac{P}{P} \\ W &= RT \log \frac{P}{p}. \quad (1, a)\end{aligned}$$

This expression connects the amount of work required to concentrate a solution, with the resulting change of its vapor pressure. Furthermore, the electromotive activity of the various types of electrical cells may be shown to depend upon a transformation of volume energy into electricity, and since this equation determines the change of volume energy it yields the theory of the cell<sup>2</sup>. The relation is a fundamental one in the Theory of Solutions and in Electrochemistry.

II. By a general application of equation (2) there may be expressed the mutual dependence of

Electricity,  
Surface energy,  
Heat,  
Volume energy.

<sup>1</sup> Van't Hoff, 1887.

<sup>2</sup> Nernst, 1889.



We will arrange the resulting equations, for subsequent reference.

For the equilibrium between electricity and surface energy :

$$\begin{aligned} O d\gamma &= -e d\pi \\ \frac{d\gamma}{d\pi} &= \frac{-e}{O} \end{aligned} \quad (2, a)$$

This expresses the relation between surface tension and electro-motive force<sup>1</sup>.

That between surface energy and heat is

$$\begin{aligned} \frac{q}{T} \cdot dT &= O \cdot d\gamma \\ \frac{d\gamma}{dT} &= \frac{q}{T \cdot O} \end{aligned} \quad (2, b)$$

an expression for the temperature coefficient of surface tension<sup>1</sup>.

For the extremely important equilibrium between electricity and heat :

$$\begin{aligned} e d\pi &= \frac{q}{T} \cdot dT \\ \frac{d\pi}{dT} &= \frac{q}{T \cdot e} \end{aligned} \quad (2, c)$$

This famous equation<sup>1</sup> introduces the element of temperature into the theory of electrochemistry.

Another relation of great importance<sup>1</sup> is obtained from the equilibrium between heat and volume energy, [(v'—v)=increase of molecular volume].

$$\begin{aligned} \frac{q}{T} \cdot dT &= (v' - v) dp \\ \frac{dp}{dT} &= \frac{q}{T(v' - v)} \end{aligned} \quad (2, d)$$

It comprehends the extremely extended theory of such changes of state as are involved in the processes of vaporization, sublimation, dissolving, melting and the transformation of allotropic forms, and is in consequence one of the most important relations in chemical theory.

All these special cases of equation (2) have the form

$$\begin{aligned} C' \cdot dI' &= C \cdot dI \\ \text{or} \quad \frac{dI'}{dI} &= \frac{C}{C'} \end{aligned}$$

<sup>1</sup> First derived in this way by Ostwald, 1892.

and they express the details of what is technically known as the Theory of "Complete" Equilibria.

III. The final division of this energy system, that dominated by equation (3), is concerned with the influence of extraneous energy forms upon the purely chemical volume energy equilibria of reversible reactions. When a system of reacting substances is in equilibrium, the total virtual change  $\sum v dp$  of the volume energy of the reaction products is balanced by that  $\sum V dP$  of the original substances.  $p$  and  $v$  represent throughout the partial pressures and molecular volumes of the substances in question, and when the system is left to itself our fundamental equation (3) assumes the form

$$\sum v dp - \sum V dP = 0.$$

With the aid of the general "equation of condition" of dilute matter,  $p v = n R t$ , whence  $p = n R T v^{-1}$  and  $dp = -n R T \frac{dv}{v^2}$ , we can eliminate the pressure factor, obtaining

$$-R T (n \sum d \log v - N \sum d \log V) = 0,$$

whence, at constant temperature, replacing the molecular volume by its reciprocal the molecular concentration,

$$\sum d \log c^n = \sum d \log C^N.$$

The integral of this equation furnishes the concentration relations for a chemical equilibrium at constant temperature,

$$\sum \log c^n + \log k' = \sum \log C^N + \log k$$

$$i.e. \quad \frac{c_1^{n_1} \cdot c_2^{n_2} \cdot \dots}{C_1^{N_1} \cdot C_2^{N_2} \cdot \dots} = \frac{k}{k'} = K$$

$$or \quad C_1^{n_1} \cdot C_2^{n_2} \cdot \dots = K \cdot C_1^{N_1} \cdot C_2^{N_2} \cdot \dots$$

which states the effect of each reacting substance to be proportional to its concentration. This is the great Law of Mass Action<sup>1</sup>, or the Reaction Isotherm, expressing the conditions of chemical equilibrium at constant temperature. Its application has brought to light a system of experimentally confirmed quantitative relations more extended than has resulted from any other law of theoretical chemistry.

If pressure be applied to a system of reacting substances work is done upon it and a deformation of its chemical equilibrium

<sup>1</sup> Guldberg and Waage, 1867.

results. The fundamental equation (3) represents this equilibrium between volume energy and work in the form

$$-\Delta v \cdot dp - (\sum v dp - \sum V dP) = 0,$$

where— $\Delta v$  is the volume decrease accompanying the reaction in question, and is a function of the specific volumes of the substances. The bracketed expression we have already found to be  $RT d \log K$ ,  $K$  being at a given temperature the constant *characterizing* the equilibrium. So we have

$$\frac{d \log k}{d p} = \frac{-\Delta v}{RT} \quad (3, b)$$

expressing the effect of pressure upon a chemical equilibrium<sup>1</sup>.

One more case remains under this head, that concerned with the influence of temperature upon a movable equilibrium. On adding the heat quantity  $Q$  to our chemical system, the resulting balance between it and the volume energy change of the displaced chemical equilibrium is, by the governing equation (3),

$$\begin{aligned} \frac{Q}{T} \cdot dT - (\sum v dp - \sum V dP) &= 0 \\ \frac{Q}{T} \cdot dT - RT d \log K &= 0 \\ \frac{d \log K}{d T} &= \frac{Q}{RT^2} \end{aligned} \quad (3, c)$$

This equation<sup>2</sup> connects the influence of temperature with the heat of reaction. Its applications to chemical phenomena have been extended and are brilliant in the extreme.

This general arrangement of the elements of chemical theory, which the energy idea leads us to adopt, takes up successively:

The Conservation of Energy,  
The Theory of Solutions,  
Electrochemistry,  
"Complete Equilibria,"  
Reaction Equilibria (including Reaction Velocities),

and includes under these heads a wealth of material really quite unanticipated by those who have not followed the results of recent research. A logical sequence has hitherto been markedly absent in what has passed for Theoretical Chemistry, and so the possibility of this coherent arrangement is a pleasing indication

<sup>1</sup> Planck, 1887.

<sup>2</sup> Van't Hoff.

that this branch of knowledge is rapidly becoming an exact science.

**Free Energy.**—Chemical action usually effects changes in the state of aggregation or in the density of the substances concerned and so produces work (or other energy forms, *e. g.* electricity, entirely convertible into work) as well as heat. A distinction must therefore be made between that part of the available energy capable of direct conversion into work and that part producible only as heat. The first is appropriately termed the Free Energy, the second the Bound Energy of the system.

A spontaneously occurring natural process is one taking up no energy other than heat from the surrounding medium. Every such process may be made to yield a definite maximum amount of work. For, if its available work were negative it would have to take place without absorption of energy, and on being reversed by the addition of heat would transform this heat into work. The operation might be indefinitely repeated, continually converting constant-temperature heat into work, a result in conflict with the second energy law.

Since every spontaneous process must yield work, a system incapable of yielding work (one whose free energy has minimum value) is incapable of spontaneous change, is in stable equilibrium. So this condition of equilibrium<sup>1</sup>, deduced from the second energy law, is

**The Decrease of Free Energy must be a maximum.**

Processes originating spontaneously and proceeding at constant temperature can take place only in such direction as to cause a diminution of free energy, a production of energy forms convertible without limit ("work"). It is therefore the decrease of free energy, and not the heat developed, which determines the direction in which chemical affinities can become active, *and which is the measure of the work-value of the chemical forces.*

Of all possible chemical changes in a material system the one involving the greatest decrease of its free energy (the maximum available work) will occur. Neither the reaction involving maximum production of heat, nor that of maximum thermal tonality

<sup>1</sup> Helmholtz, 1852.

(sum of heat and work produced) will necessarily take place; there are in fact many spontaneously occurring chemical processes which absorb heat. The decrease of free energy in any given reaction is found by determining the work to be gained when the transformation is made reversible and isothermal.

*The Equations of Thermodynamics.*—The science of thermodynamics considers the mutual transformations of heat and work. An equilibrium between them must, in accordance with the general principle of virtual energies, be expressed by the equation

$$\frac{Q}{T} \cdot dT = dW \quad (\alpha)$$

These energy differentials are equal. On changing by  $dT$  the temperature of the total heat quantity  $Q$  the fraction  $\frac{dT}{T}$  of it may be transformed into work<sup>1</sup>. This work quantity  $dW$  is the maximum available, since no heat is supposed lost. The two energies being considered exactly in balance the energy displacement in question is a reversible one.

In any such change of a material system the decrease of its total energy is, according to the first energy law, the sum of the heat and work given out, so here (reckoning, as customary, positive  $Q$  as heat *added*)

$$\begin{array}{ccccc} \text{Decrease of} & & \text{Max. work} & & \text{Heat} \\ \text{total energy.} & & \text{given out.} & & \text{given out.} \\ \text{(Thermal Tonality)} & & & & \\ U & = & W & + & (-Q). \end{array}$$

Substituting in ( $\alpha$ ) the value of  $Q$  thus given, we obtain

$$W - U = T \frac{dW}{dT} \quad (\beta)$$

an equation of great importance in chemical thermodynamics, in that it connects the decrease of the free energy (maximum available work) of a system with its total energy change.<sup>2</sup>

*The Energy Method.*—A prominent and unfortunate phase of the history of the energy doctrine deserves especial mention in this place. In the years immediately following 1870 a singular idea worked its way into very general acceptance in the scientific world. The popular hypothesis of a molecular constitution of

<sup>1</sup> Clausius.

<sup>2</sup> Helmholtz, 1882.

matter led to the conception of heat as the kinetic energy of moving molecules, and this ingenious thought gave rise to the idea that all energy forms are manifestations of kinetic energy, kinetic energy being regarded thereupon as *energy itself*. In consequence of this, each department of exact science came to be looked upon as a branch of mechanics.

This kineticism took the scientific world by storm and, by reason of the actual impossibility of adequately treating the phenomena of electricity, heat, etc., as kinetic energies, it has exerted a seriously hemming influence upon the development of rational ideas in physics and chemistry for a good twenty years. And it is lamentably true that its evil effects have not, even yet, died wholly away from among us. Nevertheless, in this day of progress it scarcely needs to be emphasized that the chief advances made in the theory of phenomena during the last half century have been made independently of this vicious assumption of discrete molecules. Physical theory and not mechanical hypothesis has been the guiding star.

The object of science is to find and classify the relations between phenomena, and to do this in such wise that their comprehension shall be unfettered by auxiliary assumptions. It cannot be too emphatically insisted upon that a distinct line of demarcation must be maintained between that which we *know* and that which is of essentially hypothetical nature. Neglect of this elemental necessity has made chemistry a strange mixture of empirical fact and wierd hypothesis. It is a necessary principle of scientific work that only a minimum employment of hypotheses is admissible—and herein lies an especially important feature of the theory of energy. In disregarding improved assumptions, such as, for example, the mechanical hypothesis of a molecular structure of matter, it deals directly with known facts and the results which it reaches are of necessity actual relations between measurable quantities. Among them are the remarkable relations which form the framework of thermodynamics, of electrochemistry, of chemical equilibrium, of the solution theory. The mutual dependence of vapor pressure and heat of vaporization, of electromotive force and heat of reaction, of reaction velocity and temperature, of the freezing point of a so-

lution and the heat of fusion of its solvent are among the most brilliant results of exact science.

This energy method, with its fruitful principle of virtual changes, is rearing the framework of a coherent theory of chemical processes, and it is through this development of a science of exact relations that we must hope to be relieved from the thrall-dom of unproven, frequently unprovable and always unnecessary mechanical hypotheses. Through this appears for the first time in the history of chemistry a prospect of dealing directly with facts as such, *and only with facts*.

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### WORK OF THE COMMITTEES ON THE "INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL."<sup>1</sup>

BY JOHN W. LANGLEY, CLEVELAND, OHIO.

THE history of the organization and work of these committees up to the present year is briefly as follows:

In the summer of 1888 it was the fortune of the present writer to present the subject of the desirability of establishing a set of samples of steel which should be analyzed with extreme care, in order that they might become standards to which scientific and commercial analyses of iron and steel could be subsequently referred; also, that greater uniformity in the results of analyses might be brought about, since these standards would bear towards analytical methods somewhat the position which the original units of weight and length, the gram and meter, or the pound and yard, do to the mechanical arts.

The plan met with hearty co-operation, with the result that committees were appointed in Sweden, Germany, France, England, and America to receive the material and see that the necessary analyses were executed.

These committees were constituted as follows:

In Sweden, Prof. Richard Åkerman; in Germany, by the authority of the minister of public works, the execution of the analyses has been entrusted to the Königl. Chemisch Technischen Versuchungsanstalt, in Berlin; in France, Mons. Ferd.

<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1893.



Gautier; in England, the British Association for the Advancement of Science; in America, a joint committee from members of the University of Michigan and of the American Society of Civil Engineers.

This latter body appointed a committee of seven analysts as follows: Andrew A. Blair, Philadelphia, Pa.; Regis Chauvenet, Golden, Colorado; Thomas M. Drown, Boston, Mass.; Charles B. Dudley, Altoona, Pa.; John W. Langley, Cleveland, Ohio; Albert B. Prescott, Ann Arbor, Mich.; P. W. Shimer, Easton, Pa.

The material for analysis at first consisted of four samples of steel prepared in this country. To this was subsequently added a fifth standard selected in England by the committee for that country.

Reports of progress have been made by the English committee in the Reports of the British Association for the Advancement of Science, volumes for 1888, 1889, 1890, 1891, 1892, the last one particularly containing a full account of the work on the four original standards.

In the United States the attention of the committee was early drawn to discrepancies caused by different methods of analysis. They therefore prepared a set of supplementary samples known as the experimental standards and to be used only in reviewing methods of analysis. A full report of their work in this line will be found in the Transactions of the American Institute of Mining Engineers, volume 19, 1890, and a brief one in volume 20.

The Swedish committee through Professor Åkerman has made a report which will be given shortly.

The outcome of the American committee's work on the modes of determining carbon resulted in calling attention to important errors likely to occur when using double chloride of copper and ammonium as a solvent for the steel owing to the great difficulty of obtaining this salt free from pyridin and other tarry products. They recommend substituting chloride of potassium for chloride of ammonium, which is found to be a complete remedy. They also found that contrary to the usual practice this solvent must not be neutral, but must be rendered strongly acid with

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from five to ten per cent. of its volume of strong hydrochloric acid.

They also call attention to the great tendency which chlorine compounds have to pass out of the combustion apparatus and to lodge in the absorption train, thus increasing the apparent weight of carbonic acid, and they give methods for arresting it.

During the past year this committee has continued its work. The communication from Professor Drown given below enumerates very fully the precautions necessary and some inevitable causes of variation in carbon determinations.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, JULY 29, 1893.

PROF. JOHN W. LANGLEY, *Chairman, Committee on  
International Standards for the Analysis of Iron and Steel*;

DEAR SIR: I give you herewith the results of my determinations of the carbon in the experimental steel standard. The sample examined was marked "hammered."

The amount of carbon found in six consecutive analyses was:

Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.050	1.057	1.054	1.030	1.054	1.053

These results were all obtained by precisely the same process and method of manipulation. The agreement is satisfactory with the exception of the fourth. I know of no reason why this result should have been lower than the others. The average of the six determinations is 1.0497. If the fourth determination is omitted, which I think it reasonable to do, the average of the remaining five determinations is 1.0536 per cent.

The process used was as follows: Three grams of the steel were treated with 200 cc. of a solution of copper-potassium chloride (300 grams to the liter) and fifteen cc. of hydrochloric acid (sp. gr. 1.2). After complete solution of the iron the carbon was filtered off on an asbestos-lined platinum boat, thoroughly washed with hydrochloric acid, and then with water until the washings gave no reaction with silver nitrate. After drying, the boat was put into a porcelain tube and the carbon burned in a current of oxygen.

The oxygen was passed over red hot copper oxide, then through caustic potash, then over calcium chloride before it entered the porcelain tube. The tube contained at its farther end several inches of copper oxide and a coil of metallic silver, which were heated to redness before the carbon was ignited.

The gases on leaving the porcelain tube were passed, first, through a small bulb tube containing an acid solution of ferrous sulphate, then over anhydrous copper sulphate on pumice, and finally over calcium

chloride before entering the potash bulb. The latter was provided with a small extension tube containing calcium chloride.

Before beginning each combustion two or three blank combustions were made to see that there was no source of error in the apparatus itself. The oxygen was swept out with air (free from moisture and carbonic acid) and the potash bulbs were closed with rubber tubing plugged with capillary glass tubes.

The silver coil, ferrous sulphate, and anhydrous copper sulphate were all used for the purpose of absorbing hydrochloric acid or chlorine. In Mr. P. W. Shimer's communication on this subject he calls attention to the fact that absorbents of hydrochloric acid are unnecessary if the acid is entirely washed out in the original filtration, an operation which would seem to be not at all difficult. I have long held the same view as Mr. Shimer, and yet I am compelled to admit that better agreeing results can be regularly and consecutively obtained if all possible precautions are taken at the time of the combustion against the entrance of chlorine or hydrochloric acid into the potash bulbs.

I am indebted to Dr. C. B. Dudley for the suggestion of the use of ferrous sulphate, and I think it a valuable addition to the process. The solution is made by adding concentrated sulphuric acid to a saturated solution of ferrous sulphate until the latter begins to crystallize out.

A series of determinations made in all respects like those given above, except that this small bulb of ferrous sulphate was not inserted, gave the following results:

Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.
1.073	1.080	1.051	1.051	1.037	1.040	1.049	1.069

There are three abnormally high results in this series, which do not appear in the series in which the ferrous sulphate was used.

In the course of this study I have made several hundred blank combustions to determine what errors might be introduced in the apparatus and manipulation. On some days there would be a constant gain in weight in the potash bulbs, on other days a constant loss, and again, at other times, the bulbs would not change in weight, in spite of the fact that the conditions of the experiments as to time, quantities of oxygen and air passed, and arrangement of apparatus were the same. On moist days, as every chemist of experience has observed, it is almost impossible to get a satisfactory weight of the potash bulbs, and it is also well known that differences of temperature between laboratory and weighing room must always be taken into consideration. The very least error, plus or minus, which one must count upon in the final weight of carbonic acid is, I think, 0.0003 gram. This can not be thought large when one considers the great weight of the bulbs, the large amount of oxygen and air (one or two liters) passing through them, the large surface of glass exposed, and the fluctuating conditions of humidity and temperature in the laboratory and weighing room. And yet this three-tenths of

a milligram amounts to 0.003 per cent. of the carbon when three grams of steel are used for the analysis. It seems to me that a variation plus or minus of 0.005 per cent. on carbon in steel is the very least that should be allowed in view of the many sources of error inherent in the combustion process as now generally used. And I am inclined to think that it would be very seldom that the variation on ten consecutive determinations would fall within this limit, even with chemists of experience in this line of work.

I have satisfied myself by many experiments that a small extension tube filled with very small fragments of calcium chloride attached to the potash bulbs is entirely adequate to collect any moisture that may be carried over from the potash solution, and that the latter does not allow any carbonic acid to pass through. The use of solid caustic potash in the extension tube is therefore unnecessary. Neither have I found any advantage in the addition of a drop or two of water in the bulb of the calcium chloride tube to moisten the air after it has passed the anhydrous copper sulphate.

In addition to the work above given I have made a large number of determinations of the carbon in the experimental standard under different conditions. Some of the results thus obtained it may be worth while to record. A determination made in the same series as those first given, and in precisely the same manner, except that copper-ammonium chloride was used instead of the potassium salt, gave the per cent. of carbon as 1.053. This would indicate that the ammonium salt can be safely used when free from carbon.<sup>1</sup> That cupric chloride acidified with hydrochloric acid can be used for the solution of the iron has already been shown by other members of the committee. I have made several experiments in this direction with the view of using this method exclusively, and thus avoid the necessity of using a crystallized double salt of copper. Cupric chloride acidified with twenty per cent. of strong hydrochloric acid dissolves iron with reasonable promptness and gives good results. The addition of forty per cent. of hydrochloric acid is apt to cause loss of carbon. But hydrochloric acid is not as good a solvent of cuprous chloride as the alkaline chlorides.

It seemed obvious that the addition of potassium or sodium chloride to the acidified copper solution would give as good results as a solution of copper-potassium chloride. Several determinations made in this way gave fairly good results. Copper oxide, containing some metallic copper, was dissolved in hydrochloric acid, chlorine gas was passed into the solution to oxidize the cuprous chloride, and the solution was then evaporated to small bulk to expel the free chlorine; it contained some free acid. The amount of copper in this solution was determined by the battery in order that the proper amount should be used in dissolving the steel. Three grams of steel were treated with an amount of this solu-

<sup>1</sup> This copper-ammonium chloride was obtained from Messrs. Baker and Adamson, Easton, Pa.

tion which contained twelve grams of copper, fifteen cc. of hydrochloric acid (sp. gr. 1.2) and sixty cc. of a solution of common salt containing 320 grams to the liter. The steel dissolved readily. The filtration of the carbon and the combustion were made precisely as above described with all the precaution for the interception of chlorine and hydrochloric acid. The results obtained for the carbon in three experiments were:

Per cent.	Per cent.	Per cent.	Average per cent.
1.055	1.043	1.059	1.052

. A similar experiment, using potassium chloride instead of sodium chloride, gave 1.051 per cent. carbon.

I have also made a large number of experiments with silver sulphate as a solvent for the steel, but I did not obtain any satisfactory results in this way.

I take pleasure in acknowledging my great indebtedness to Mr. Wm. S. Davenport, instructor in analytical chemistry in the Massachusetts Institute of Technology, for the analytical work of this investigation, and for many valuable suggestions regarding the processes employed.

THOMAS M. DROWN.

The original four standards have now been analyzed in three countries with the following result.

The English committee give as the mean of their determinations:

#### ENGLISH COMMITTEE.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon .....	1.414	0.816	0.476	0.151
Silicon .....	0.263	0.191	0.141	0.008
Sulphur .....	0.006	0.007	0.008	0.039
Phosphorus .....	0.018	0.014	0.021	0.078
Manganese .....	0.259	0.141	0.145	0.130

The Swedish committee through Professor Åkerman give their means as:

#### SWEDISH COMMITTEE.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon .....	1.45	0.84	0.50	0.17
Silicon .....	0.257	0.185	0.15	0.015
Sulphur .....	0.008	0.004	0.006	0.048
Phosphorus .....	0.022	0.015	0.021	0.102
Manganese .....	0.282	0.145	0.17	0.13

The American members have not held a joint meeting this year and there are one or two analysts who have not completed

their work, so that the averages given below may suffer some small modification in the future.

## AMERICAN COMMITTEE.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon .....	1.44	0.807	0.452	0.16
Silicon .....	0.270	0.202	0.152	0.015
Sulphur.....	0.004	0.004	0.004	0.038
Phosphorus .....	0.016	0.010	0.015	0.088
Manganese .....	0.254	0.124	0.140	0.098

The German committee has devoted much attention to the study of methods of analysis in connection with the international standards, but has not yet announced its results. The French committee has made no report.

## STANDARDIZING THE TORSION VISCOSIMETER.

By O. S. DOOLITTLE, CHEMIST, P. & R. R. Co.

Received October 24, 1893.

IN the article published in the June number of *Drugs, Oils, and Paints*,<sup>1</sup> on the Torsion Viscosimeter, the method recommended for expressing the viscosity was in the number of degrees of retardation between the first and second complete arcs. Further experience has shown that although this is the best method for any one instrument, yet when it comes to comparing different instruments it is too delicate. It has been found that two instruments cannot be made to show the same number of degrees of retardation throughout a wide range of viscosity without requiring an amount of care and exactness in the manufacture which greatly adds to their cost.

In order to overcome this difficulty each instrument is now standardized against pure cane sugar solutions, after the manner proposed by Mr. S. M. Babcock (*J. Anal. Chem.*, 1, 151,) in a similar case, the viscosity being expressed in the number of grams of sugar contained in 100 cc. of the syrup at 60° F., which will give the retardation designated at 80° F. These readings are obtained by taking a number of solutions contain-

<sup>1</sup> See this JOURNAL, March, 1893.

ing known amounts of pure cane sugar, and determining the retardation of each. A curve is then mapped out on a piece of plotting paper, the number of grams of sugar in 100 cc. of the different syrups representing the abscisses, and the degrees of retardation, the ordinates. This curve enables us to interpolate the value of each degree of retardation in terms of pure cane sugar, and in this way a table of viscosities is drawn up and furnished with each instrument. This table renders the results obtained by different instruments strictly comparable.

Incidentally while experimenting with these sugar solutions I have been able to show the influence which specific gravity has on the determination of viscosity, when made by the class of instruments which allow the liquid to flow through an orifice, and express their results in the number of seconds required. The viscosity on the torsion viscosimeter of a certain oil having a specific gravity of 0.9 was found to be 86.4. I then made a sugar solution showing exactly the same viscosity, and found its specific gravity to be 1.4. These two liquids having identically the same viscosity as shown by the torsion viscosimeter but differing in specific gravity, were then run through the Saybolt viscosimeter. The oil required  $35\frac{1}{4}$  seconds, while the sugar solution ran through in  $30\frac{1}{4}$  seconds, thus showing that the difference in specific gravity caused an error of five seconds on this instrument by forcing the sugar solution through the orifice faster than the oil. To demonstrate still further the presence of this error, the viscosity of an oil of 0.9 sp. gr., was ascertained to be  $35\frac{3}{4}$  seconds on the Saybolt instrument. I then made a sugar solution which gave exactly the same figure on this viscosimeter, showing a specific gravity of 1.48. The viscosity of these two liquids was then taken with the torsion viscosimeter, when it was found that the oil showed a viscosity of 86.8, while the sugar solution gave 91.8. In other words it was necessary to make a solution of sugar of decidedly higher actual viscosity than the oil, in order to overcome the error due to difference in specific gravity and show the same reading on the Saybolt viscosimeter.

From this it would seem clearly evident that the viscosity as determined by any instrument based on the principle of allowing

the liquid to flow from a receptacle through an orifice, has a very appreciable error due to the specific gravity of the oil.

The torsion viscosimeter is manufactured and sold by Bull-ock and Crenshaw, 528 Arch street, Philadelphia.

### PROGRESS IN THE MANUFACTURE AND USE OF ARTIFICIAL COLORING MATTERS.<sup>1</sup>

BY OTTO N. WITT, PH.D., PROFESSOR AT THE POLYTECHNIC INSTITUTE OF BERLIN.

HAVING been requested to deliver an address before this congress, I know of no better subject to call your attention to than the one with which I have been familiar from the beginning, the chemistry of artificial coloring matters and their relation to dyeing and calico printing.

Unfortunately the subject is one of such vast dimensions, that I should fail to give you anything like a complete description of it, even if I could venture to trespass much longer upon your valuable time than it is my intention of doing. I had to choose a certain chapter from it, and in so doing I have preferred, mindful of the eminently practical turn of this country, to bring before you rather the practical side of the recent development of coloring matters, than the theoretical one. Thus I shall avoid among other things the use of complicated structural formulas which, though indispensable to the modern organic chemist, are apt to be looked upon with disfavor by no small number of eminent and accomplished chemists.


The question of artificial coloring matters is, I am sorry to say, one which has hitherto been left entirely in the hands of the chemists of the old world, who, I need not assure you, would be only too glad to collaborate in this matter as well as in so many others, with their colleagues in the United States. But it seems that quite peculiar conditions are required to develop this particular flower on the vigorous and imposing tree of general chemistry and we have, even in the old world, noticed the remarkable fact that the industry of artificial dye stuffs, born in France, has left that country to settle in England; and here again it has not been able to reach its full development, but has

<sup>1</sup> Read before the World's Congress of Chemists, August 21, 1893.

preferred, with no apparent cause, to make the German Empire its final emporium. But here at last it has grown to such imposing magnitude, that the world has now, for more than a decade, been ringing with its praise and admiration. And this praise has not been bestowed with injustice. The whole life and thought of some of our greatest scientists have been spent in considering and mastering the intricate problems connected with the chemistry of aromatic compounds, to which all synthetic dyestuffs belong and every progress of the manufacture of these interesting substances has been the result of masterly work in the domain of pure science. The method, now so generally recognized, of applying scientific principles to every practical question, however trivial it may at first seem to be, has never been more successfully adopted than in the manufacture and use of dyestuffs, where nothing may be guessed or discovered, but everything concluded and invented.

The new brilliant era in the chemistry of artificial coloring matters was inaugurated by the discovery of the law, which governs the connection of the chemical constitution with the properties of artificial dyestuffs. It would lead too far to set before you on this occasion these laws themselves and to expound the many examples of their correctness and universal applicability. But it is quite natural, that, when once these laws were established, the production of dyestuffs ceased to be the result of lucky circumstances and became the object of profound and in many cases brilliant logical argument, and thus it is that to-day coloring matters may be produced by thousands, all of which are absolutely and perfectly new and the properties of which may be established with perfect certainty before even the smallest sample of them has ever been prepared. So great is the number of new dye-stuffs for the production of which we have every means at our disposal, that it seems quite impossible that all of them will ever be prepared even as laboratory specimens.

Now it will be easily seen that science whilst placing a treasure of such imposing magnitude at the disposal of the manufacturer, has not only benefitted him, but that she has also vastly increased his work and responsibilities. And thus we see the






old fashioned factories, such as I remember them from the days of my youth, consisting of a few sheds and a snug little laboratory, replaced by the enormous places which now serve the same purpose and of which you may see an excellent representation in the exhibition of the German chemical industry in the World's Fair; places resembling towns or cities, consisting of hundreds of buildings of vast proportions and over-shadowed by dozens of huge chimneys; with laboratories much larger than those of the most renowned universities, and in which hundreds of chemists and assistants are constantly at work; and in the workshops themselves the few casks and stirrers which used to be the main implements of the manufacturer of dye-stuffs, have been replaced by costly machinery, too varied and complicated to attempt its description.

Now it seems natural to ask whether all this is but temporary or lasting; or, in other words, whether such complicated means for the production of artificial dye-stuffs will forever be necessary or whether, in the near future to come, all this may not be much simplified. It seems but natural to start from correct scientific principles and to conclude that we do not want such a large number of dye-stuffs as we are actually capable of producing. We know that there are a few primary colors from which all the other shades may be produced by mixture. Why not, therefore, select amongst the vast number of dye-stuffs at our disposal a few which, whilst being cheap and easy of manufacture, represent our primary shades. Let us then dye everything with these and neglect the rest, from a practical point of view. This seems sound reason, and the enormous apparatus which is at present used by the manufacturer seems to involve an unnecessary complication.

I regret to say that this way of looking at the subject proves quite erroneous if we examine it a little more closely. The simple laws of the combination of colors in the physical sense of the word are not applicable to dye stuffs used for dyeing textile materials. Coloring matters of given shades may be blended together, but it is impossible to produce, by their mixture, shades of such freshness and purity as the same shade produced by one individual chemical compound would possess.




It is easy to explain the causes of this fact, but in order to be brief we will take it as granted, and we will then see at once why such a large number of intermediate shades have to be prepared. Thus, for instance, a careful silk dyer would never think of producing a purple from a mixture of blue and red, although physically this would seem possible. He would always, to insure a good result, use any or either of the purple dye stuffs now in the market. I may say that there are at present about thirty different purples sold, and that no one of them is a mixture but a well-defined individual compound of different shade and properties.

But the color which may be produced on a textile material by a certain dye-stuff is not the only point to be considered in using this dye-stuff. Here we come to the most interesting side of the question—to the relation between the coloring matter and the process of its application.

What is the process of dyeing? This is a question which has for a long time puzzled the minds of many scientists. It is now generally admitted that it is a chemical process, a process of actual combination between the substance of the dye-stuff and the substance of the fiber. But the impossibility of establishing in the majority of cases any molecular proportions in the chemical reaction which is taking place has for a long time been the stumbling block of those who wished to examine this reaction more closely. It is only quite recently that the true nature of the process has been recognized. Dyeing is certainly a chemical process, but one of those in which simple molecular proportions can no longer be established. These processes have of late been more closely investigated, and we now comprise them under the heading of solutions. If I dissolve sugar in water, a chemical reaction, a combination of the two ingredients takes place, and the solution formed is a chemical compound, whatever be the proportion of its constituents. And the same rule applies in a great many other cases.

The difficulty in grasping the true scientific sense of the word "solution" lies in the fact that we have from our childhood been accustomed to consider a solution as something liquid. This is by no means a necessity, and there are quite as many



solid solutions as liquid ones. To give you an example I will take blue glass. This is a solution of sodium-cobaltic silicate of an intensely blue color in colorless normal crown or flint glass. Both the constituents of this solution are solids, and so is the solution itself; still the two compounds in combining together do so according to exactly the same principles as sugar and water in producing a liquid solution.

Without going into details I may state that every dyed fiber may be looked upon as a solid solution of exactly the same character as blue glass. Its mode of formation is different, but the result is none the less the same.

Taking this as established, we may at once draw an interesting conclusion. If for dissolving sugar we take spirit instead of water we find at once that sugar is much less soluble in this medium. Now there is quite as much difference between silk and cotton as there is between spirit and water, and thus we understand why the different textile fibers can not be dyed with equal facility. The chemical substance of the fiber being the solvent for the dye-stuff, it is but natural that its solvent power should not be equal in all cases. Thus it is that we have to use different dye-stuffs for the various textile fibers, and, as the number of the latter is rather on the increase than the reverse, we shall have to meet in the future a demand for an increased variety of the dye-stuffs produced.

The discovery of the true relation between the dye-stuff and the fiber has coincided with some of the most important forward steps in the industry of artificial coloring matters, and in some respects has been instrumental in facilitating such progress.

The majority of the older dye-stuffs have been remarkable for their solubility in, or, as the chemists of the old school would express it, for their affinity for silk and wool rather than for cotton and the other cellulose fibers. In applying them to cotton certain artifices had to be used, known as mordanting, processes into the nature of which we need not enter, but which made the dyeing of cotton both difficult and expensive. But when we remember that the relation of the two solvents, spirit and water, to sugar is not a universal one; that there are a great many substances which dissolve easily in spirit and spar-

ingly or not at all in water, we see at once that there is no reason why the same should not apply to dye-stuffs and why there should not be dye-stuffs which, contrary to those hitherto produced, dissolve more easily in cotton than in silk or wool. If such dye-stuffs could be produced, their production would of necessity represent an immense progress in the dyeing of all vegetable fibers, of which, as you are aware, about ten times as large a quantity is consumed all over the world as of silk and wool taken together.

Well, this progress was realized about eight years ago, when the first synthetical dye-stuff more soluble in cotton than in animal fibers was put on the market under the name of Congo. This compound dyes cotton a brilliant scarlet without the use of a mordant. Ever since its discovery many chemists have been at work inventing new dye-stuffs which, whilst being endowed with the same important property, would supply the other shades, and at present we have several hundreds of them, dyeing every shade of the spectrum and placing the cotton dyer on the same convenient footing with the silk and wool dyer. I need hardly add that the relations between the constitution of these dye-stuffs and their interesting new properties have been fully cleared up, and that the production of all the varied shades of this new class of coloring matters is the result of truly scientific and logical work, and not in the least that of lucky chance.

There are many more things of general interest which I might bring before you, but I prefer to limit myself to the discussion of but one more important subject.

This important subject is the question of the fastness of artificial dye-stuffs, of their power of resistance to the chemical action of the various conditions to which a dyed textile fabric must of necessity be exposed.

I may state at once that there are few things in chemistry about which so many and such unfounded popular prejudices are afloat as this question of the fastness of artificial coloring matters.

It is true that the first synthetical dye-stuffs placed on the market, magenta and its derivatives, were of a rather fugitive

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character. But there is no logical connection between this unfortunate fact and the artificial production of the substances to which it applies. If by some chance we should discover that magenta occurs as a natural constituent of some gorgeously colored flower or fruit, it would be equally fugitive; whilst alizarine and indigo, when prepared by artificial means, showed themselves quite as fast and permanent as when extracted from the plants in which they occur. In fact, I need not point out to an assembly of chemists that there is no barrier which divides natural coloring matters from artificial ones, that permanent and fugitive substances occur in both groups, and that it is the task of the colorist to make a proper selection amongst them. But in order to be able to make such a selection he requires a very large stock to choose from, and thus modern organic chemistry in placing at our disposal an overwhelming number of new coloring matters has conferred upon us a boon which can not be over estimated,—the possibility of choosing our dyeing materials not only according to the beauty of their shade, but also according to their more hidden, inherent value. We possess now artificial dye-stuffs of such a degree of permanence that neither indigo nor any other of the most renowned old natural dye-stuffs can even approach them. Most interesting and severe tests have been made which prove this beyond any doubt, and I can only invite you to look at the specimens illustrating these tests and exhibited in the collective exhibition of the German chemical industry in the Manufactures Building.

The researches on the permanence of artificial dye-stuffs, which have yielded these important results, have also been instrumental in exposing another silly and illogical popular prejudice. This prejudice consists in the belief that all bright and brilliant dyes are necessarily of a fugitive nature and that on the other hand permanent coloring matters are invariably of sombre and subdued shades. Recent researches have shown that no such relation exists between the brilliancy of dye-stuffs and their fastness. Whilst both these properties are functions of the constitution of dye-stuffs, there seems to be no inherent connection between them. And thus I may confidently recom-

mend to the ladies among this audience to continue the use of bright and pleasing colors without any fear of their being fugitive merely on account of their brilliancy. Rhodamine, the new pink, surpassing in its beauty even the delicate leaves of the rose, is not only a brilliant, but also a fast color, and it does by no means stand alone amongst modern artificial dye-stuffs in combining these two most valuable properties.

And now, ladies and gentlemen, I will not trespass upon your time any longer. My sketch of the recent progress in the chemistry of artificial dye-stuffs has of necessity been short and incomplete; but if I have succeeded in convincing you that this domain of organic chemistry has not been lying dormant of late and that all its progress has been the result of laborious and difficult, but in its final results, brilliant and successful scientific work, I shall consider myself amply rewarded.

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### HOW CHEMISTRY IS BEST TAUGHT.<sup>1</sup>

BY CHARLES F. MABERY.

THE subject, "How Chemistry Is Best Taught," which has been proposed to us for discussion, has a serious interest for all persons who are engaged in teaching chemistry, and it is of especial importance to those of us who have in charge the preparation of young men for professional employment. In view of the prominence of scientific subjects and methods in the present systems of education, it is incumbent upon the adherents of these methods to demonstrate by their results that they are not in error in assuming that science should have an equivalent place with other departments of knowledge. In the higher institutions this question has received a definite answer; in the secondary schools evidently much has yet to be accomplished in the direction of general education as well as in the preparation for higher study.

That the importance of a knowledge of elementary chemistry is apparent to all who are capable of appreciating its usefulness is evident in the recent extension of instruction in the secondary

<sup>1</sup> Read before the World's Congress of Chemists, August 26, 1893.



schools. In the larger portion of our high schools, however, physical science still occupies a subordinate place, or it is taught merely from text books with little if any laboratory training. Probably the chief hindrance to any radical change is a lack of appreciation on the part of the public. If parents could be brought to see that their sons and daughters would receive a better education if physical science properly taught formed an essential feature of the high school course the change would not be long delayed. That the training of many teachers is scarcely more comprehensive than they are called upon to impart is of less importance, since at present those who are educated in the higher institutions have better opportunities and those who are deficient can improve their knowledge in special courses for teachers. Doubtless the many popular movements of the present day will exert a beneficial influence in extending an acquaintance with the application of scientific principles. Such unique and instructive object lessons as that which has been designed under the direction of Professor Ellen H. Richards for the Rumford kitchen in the Columbian Exposition can not fail to attract public attention. It requires no particular training in observation to recognize the difference in food value between a plate of Boston baked beans and an equivalent weight of potatoes; but when an appetite whetted to the sharpest edge in an endeavor to see all the exhibits in the Liberal Arts Building in one visit, and the unavailing efforts to extract a crumb of comfort from the places so improperly named, is brought in contact with the wholesome dishes prepared in the Rumford kitchen and their satisfying influence, the numbers representing the food values will be in a favorable connection to awaken a desire for further information. The same principle is applied in a different manner in the exhibits from the agricultural stations which explain the composition of dairy products, of animal foods, and the methods of chemical investigations. Such exhibits have a particular interest for persons engaged in agricultural pursuits, since they are a part of the well-directed efforts of the stations in disseminating knowledge. Probably in no department of education has there been a more substantial growth during the last twenty years than on the part

of intelligent farmers in applying the practical information coming to them from the results of investigations carried on at the experiment stations. These illustrations may seem somewhat removed from the main question before us, but I am convinced that the efficiency of higher instruction in chemistry will be greatly improved when students coming to us from the secondary schools shall have had the advantage of practical training in elementary physical science, and I believe this will be the sooner accomplished through a recognition of its benefits in the affairs of every day life.

I think we shall all agree that the best argument to be urged in favor of a prominent place for chemistry in any grade of instruction is the value of experimental methods for the development of mental power. This feature should naturally appear with especial prominence in courses leading to the degree of bachelor of arts; and if the schools of science are to be maintained on a higher plane than the trade schools or shops, the courses of study must be conducted with reference to the attainment of mental discipline and scholarship. In the courses in chemistry I am unable to see why this should interfere with the acquisition of practical knowledge.

The guiding star to successful teaching in chemistry is the personality and enthusiasm of the instructor. With the great increase in attendance in many institutions the earlier relations between student and instructor, which were frequently mingled with deep personal feeling somewhat akin to veneration on the part of the student, are well nigh impossible. Nevertheless, an enthusiastic teacher with tact and good judgment has little difficulty in maintaining a profound interest even in large classes. In successful teaching we all know how much depends upon the attitude of the instructor toward his students. Courteous relations with a clear understanding that teacher and students are mutually interested in the acquisition of knowledge readily secures the confidence and esteem of a body of students and the instruction need seldom be interrupted by questions of conduct. A faithful teacher does not limit his attention to the brighter minds; students slow in comprehension but earnest in application secure a store of information which will be used



later to the best advantage. It was a wise teacher who said: "I am faithful in my duty to dull students; in my old age I may need favors of the men of wealth."


In assimilating their methods from European laboratories, the chemists of the United States, untrammelled by traditions and unrestrained by the influence of any particular school, have been in favorable conditions to appreciate the labors of the great masters of other countries. Unfortunately it may be, in the wonderful development of our natural resources, the temptation to enjoy material benefits may have retarded the growth of original investigation; yet looking toward the future the erection of so many large laboratories can not fail under judicious control to contribute to the advancement of knowledge. A marked individuality in our methods is apparent even in a casual inspection of American laboratories. Variation in details is a natural consequence of differences in the temperament of different peoples; and teachers educated abroad have perceived the necessity of adapting the methods in which they were trained to the peculiar conditions.

It is with some hesitation that I approach that aspect of our subject which relates to the details of methods, since the best success in teaching is so dependent on the personality of the instructor that it would seem presumptuous to suggest a rigid scheme for all. There are certain principles at the foundation of successful teaching, however, which may properly be presented for consideration. I have already alluded to an unsatisfactory condition in the methods employed in the secondary schools. In some of the high schools, as we all know, there are teachers who are thoroughly imbued with the spirit of scientific study,—would there were more of them. Yet competent teachers are often limited in their efforts by a heavy burden of other work, or by a need of the necessary appliances. There can be no question that the high school courses would be benefited if every pupil received systematic training in elementary physical science, and I believe it is consistent with due attention to other subjects, and that it can be accomplished without any unreasonable pecuniary burden. As an expeditious and effective method for teaching chemistry in the high

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school, I would have the teacher meet the class before the lecture table, and demonstrate, experiment, and explain, simply as a convenient mode of teaching classes as one pupil should be taught. The experiments should be repeated by the student in the laboratory under the immediate oversight of the teacher, with the note book close at hand. A text book is necessary to give information which the teacher has not time to include; but no text book can supply the need of personal teaching. Occasionally teachers with limited knowledge are led to adopt methods of questionable utility by the arrangement of certain text books. Some years since a teacher in one of the high schools in the east, in which little attention was given to laboratory work for students, remarked that his pupils must have a thorough knowledge of valence and structure symbols. The topical arrangement of the subject may be left to the discretion of the teacher and the quantity to the length of time available; but it should never be forgotten that the educational value of such instruction depends upon the development of skill in manipulation, of correct habits of observation and in recording notes, and of the true spirit of scientific thought. Whatever of practical information may be included will enhance the utility of the instruction.

In the higher institutions the first course is general and descriptive chemistry, of which every person who expects to engage in any scientific pursuit should have a thorough knowledge; and, as has been suggested, this subject should have a suitable place in college courses. Concerning details of the most efficient methods in teaching general chemistry, no doubt an extended course of experimental lectures closely connected with laboratory practice affords the best training. The ground can be fairly covered in seventy or eighty lectures with four to six hours a week of laboratory work so arranged that the lectures of each week shall include the experiments for the laboratory. Weekly recitations on the subjects of the lectures and laboratory work enable the instructor to control the progress of his students. When students first enter the laboratory it is essential that they be impressed with the necessity of accuracy in the details of experimental work. This important lesson



may easily be taught by means of experiments capable of affording quantitative results. By some instructors such experiments are occasionally introduced throughout the course with the same object in view. There should be sufficient instruction in the laboratory for careful oversight of the experimental work and the note book of each student. Moreover, I am convinced that it is unwise in any grade of undergraduate study in chemistry to allow students in laboratories without constant supervision. When left to themselves they are apt to loiter, to contract careless habits, and to waste material.

Then a laboratory is held responsible for accidents, even though they occur through inexcusable carelessness of students. Every instructor in charge of a laboratory will no doubt recall heedless moments on the part of students. Some years ago, just as I entered my qualitative laboratory one day when the assistant was out of the room, I observed a student inflate his lungs twice from a bottle containing a freshly charged solution of hydrogen sulphide. He immediately fell into the arms of a companion, and it was some time before he recovered. Probably another inhalation would have proved fatal. This fellow was a sophomore, having taken one year in general and descriptive chemistry. He was fairly bright and had been using this reagent during several months. But some question arose as to the odor of the unadulterated gas, and forgetting the precepts of his freshman year, he attempted by a direct experiment to ascertain the truth.

What has been said concerning the personality of the instructor applies perhaps in a more restricted sense to the student. While methodical habits are to be strenuously insisted upon, the methods may be sufficiently flexible to allow the student to reach his conclusions in his own particular way; the particular form of the lecture and laboratory notes, for example, can be left to the preference of the student provided they are well written and complete.

For other students than those who desire special training in chemistry or in allied subjects an extended course in general and descriptive chemistry provides ample knowledge of this subject. Analytical chemistry is next in the sequence of studies

and for evident reasons qualitative analysis is first undertaken. On account of its great disciplinary value, I regard this subject as one of the most important in the whole course of chemical training. It enables the instructor constantly to test the faithfulness and proficiency of the student, and beside the mental discipline, the student acquires a comprehensive knowledge of methods of separation and identification, which is the foundation of quantitative analysis. Elementary theoretical chemistry or chemical philosophy may be conveniently and profitably taught at the same time with qualitative analysis, especially since a familiarity with stoichiometry and chemical reactions is essential in a good understanding of quantitative methods.

Thus far in teaching chemistry probably the methods are not materially different in the college and the technical school. Indeed, in the more advanced subjects, the principal difference is in the attention which should be given to the acquisition of practical knowledge in the technical courses. The methods of quantitative analysis are well adapted for the development of skill and dexterity in accurate manipulation, and to the chemist they are indispensable. As a preparation for professional employment the training in methods should be sufficiently comprehensive and thorough to enable the student to appreciate the conditions of any analytical problem; and further, I deem it of much importance that students have practice under guidance in all typical standard methods. It is not sufficient that men shall have been carefully trained in methods which impart skill and accuracy; it seems more desirable, for example, that men who enter the iron and steel industry shall be thoroughly familiar with the standard methods of iron analysis than to rely upon skill and general knowledge to acquire the special features in actual practice. The first lessons to be learned in the quantitative laboratory are accuracy and confidence; the importance of a close economy of time and effort must be appreciated, and an intelligent student will soon perceive the numerous ways for conducting analytical operations rapidly without haste. When a chemist assumes the duties of a position, every motion has a pecuniary value, and results are demanded in the smallest limit of time. This requirement is sometimes urged in favor of undergraduate training in rapid


methods. While some practice in this direction would without doubt be serviceable, in three terms at most which can be devoted to quantitative analysis the time is fully occupied in gaining a familiarity with methods, and in passing from one analysis to another the conditions are not favorable for commercial rapidity. As in actual practice, it is only possible to attain to the highest degree of accuracy and celerity when the attention of the analyst is limited to a moderate number of determinations which are continually repeated. Experience shows that well-trained students are not slow in acquiring commercial dexterity even to reporting the percentage of carbon within five minutes after a ladle of steel is poured into the mould, or a complete analysis of blast furnace slag within thirty minutes. If attempts were made to give such practice to students, there would still be much to learn in the different conditions in the laboratory of the manufacturing plant.

A branch of our subject, which has doubtless occasioned some of us much perplexity in our endeavors to give it a suitable place in an undergraduate course, is organic chemistry. Our difficulty is partly due to the feeling on the part of certain students when they have gained a good acquaintance with quantitative analysis, with the consciousness that they can secure some pecuniary return from their attainments, that they have learned all of chemistry that can be of service to them. Usually such students may be made sensible of their error, although, unfortunately, the importance of a broader view is not always appreciated until a knowledge of this subject is needed in professional occupation. That organic chemistry is a difficult subject students are not long in perceiving. It is not sufficient in a course of lectures that the principles and methods are understood; they must be learned. The importance of a broad and thorough training in theoretical and descriptive organic chemistry as a part of a chemical education is beyond question. As a part of the preparation for technological and applied chemistry, organic chemistry can most conveniently be placed in the third year; yet without some introduction I have found this subject too difficult for third year students. The plan which I have adopted with satisfactory

results includes recitations in the first term of the third year from an elementary text book with the following lectures extending throughout the second term and the first term of the fourth year. So far as possible, laboratory practice should accompany the lectures, although from the pressure of other work the greater portion of the experimental work may be pushed forward into the fourth year. In connection with the lectures students should be required to extend their knowledge by reading, and recitations are necessary to ensure faithful application. With this arrangement the principal laboratory work of the fourth year includes organic chemistry and chemical technology, assaying, gas analysis, and such other special subjects as may seem expedient can be provided for here. A course of lectures in metallurgy is of advantage to students in chemistry, and they may be attended during this year. Some additional instruction in theoretical chemistry can be given with profit.

For the utilization of chemical skill the field of manufacturing or applied chemistry is full of promise, although in this country it has largely to be developed. Suitable preparation for industrial occupation demands thorough training in the directions already suggested, and beside a good knowledge of technical processes with the aid of laboratory work so far as it is feasible to experiment with these processes on a laboratory scale. Concerning the best methods for teaching this subject, no doubt courses of lectures supplemented by reading are to be preferred, especially if part of the lectures can be given by persons engaged in professional pursuits. Several recent compilations in a convenient form for the use of students are a valuable aid.

The range in laboratory work is of necessity somewhat limited. It must consist principally in the preparation of chemical products from crude materials, in the study of mordants and dyes, and in testing the efficiency of certain features of industrial processes on a laboratory scale. The preparation of theses or written accounts of various processes should also form a prominent feature of a course in technological chemistry. Institutions fortunately situated near manufacturing establishments afford valuable opportunities to students who are enabled




to study industrial methods in actual operation. Such instruction supplemented by laboratory practice constitutes the best possible education in applied chemistry that an institution can provide.

Any discussion of the details of a chemical education must be incomplete without some reference to related subjects, either such as are closely allied to chemistry, or those which are essential in the proper mental development of every well educated person. Evidently this portion of our subject may be considered from more than one point of view. In a course of four years in the school of science there should be thorough training in mathematics so far as Calculus, and it can be no disadvantage to make a certain portion of this subject required or optional. Every chemist who aspires to a position beyond that of an analyst will be called upon to plan and oversee the construction of appliances and buildings; in fact, ingenuity and mechanical skill may occasionally be as serviceable as chemical knowledge. There are, therefore, good reasons for the acquirement by every student of a good understanding of mechanical drawing and of elementary mechanics, and this may have led to the foundation in several institutions of a course in chemical engineering. No doubt this course is in demand by persons who desire proficiency in the engineering features, but students who expect to engage in applied chemistry can hardly afford to omit any portion of the undergraduate training in chemistry. Nothing need be said as to the importance to all chemists of thorough discipline in descriptive physics with laboratory practice. A familiarity with the principles of heat and electricity with the manipulation of electrical currents are among the more important requisites. The rapid growth of electro-metallurgy indicates large possibilities for the application of electrical energy in this form, and it can evidently be best undertaken by the chemist who possesses a good knowledge of electricity. The literary training in scientific courses is usually limited to the English branches and the modern languages. Without a certain acquaintance with the latter the chemist would be seriously restricted in the sources of his information; and, moreover, to scientific students it would seem that the French

and German languages should be taught as much at least for mental discipline and culture as for their practical usefulness. Of the importance of thorough discipline in the English language and literature, history, logic and political economy, it is not necessary to speak. Determinative mineralogy may be provided for in the second or third year. Courses in agricultural or pharmaceutical chemistry, or in other special fields, should differ in the details of the third and fourth years from the course outlined above.

In college and university courses theoretical chemistry and chemical literature receives more attention, and in general less attention is given to practical applications. I do not accept the idea sometimes expressed that original investigation should not be attempted outside of the university. We are all too well aware of the difficulties in the way of carrying on special study in connection with the responsibility of undergraduate courses; and yet I am sure we appreciate the influence of such work in the atmosphere of the laboratory, as well as upon the instructor himself. Then there are always in the laboratory bright students who are able to undertake with profit the study of special problems. As a part of the preparation for teaching I look upon a certain acquaintance with the methods of original research as an essential attainment. I do not intend to assert that without it there can be no good teachers; but it certainly strengthens the equipment of a teacher who aspires to a high position.

Earlier in this paper I endeavored to give an outline of what seems to be the principal objects to be kept in view in teaching chemistry as an educational subject. Students continue in chemistry with the intention of securing professional employment either in teaching or in applied chemistry. How often are we met with the question as to what is the prospect of employment after graduation; whether the inducements are more promising in teaching or in practical fields. Concerning teaching as a profession the reply is easy. A person with an aptitude for teaching and with broad training has little difficulty in securing a position commensurate with his attainments, especially at present with the wonderful extension of our educational





institutions. But the number of positions is limited and there are few vacancies. If they were abundant not all persons even with the best possible preparation would succeed in teaching chemistry. In applied chemistry the conditions are not the same. With our enormous stores of natural products yet undeveloped, vigorous enterprise in business operations, and great industrial wealth, there can not fail to be rapid developments in the fields of manufacturing chemistry. Within the ten years just elapsed we have witnessed great changes; manufacturers who ten years ago conducted their operations almost without the aid of chemical skill now employ several chemists. Eight years ago I visited a large plant for the manufacture of sulphuric acid which contained neither a Glover nor a Gay Lussac tower. Further improvements which are necessary for the production at home of the chemical products that are now imported in large quantities require broad qualifications with extended experience; if our graduates are not sufficiently well trained, chemists will be secured elsewhere.

If there are portions of the educational field in chemistry which appeal to us with greater force than others, perhaps the elementary teaching in the secondary schools and the advanced study in preparation for teaching or for positions requiring independent skill and originality in methods are worthy of attention. The recent growth of knowledge within special fields has introduced new features into methods of instruction. In addition to courses which are adapted for all students, those who intend to undertake investigations in any particular direction should have training under the guidance of a specialist in that field. There are many economic problems of the utmost importance awaiting solution, which require not only the application of all accumulated knowledge, but the discovery of new methods. The maintenance of a healthful water supply and the economic disposal of sewage are serious problems for the present generation, and the engineer must be aided by the best skill of the chemist and of the bacteriologist.

Every laborer is directly interested in the promotion of investigations on an economic and healthful food supply. To the great army of workmen who are struggling to support families

on incomes of three or four hundred dollars a year it is a matter of serious importance to secure the best nutrition at the smallest cost. Yet it is rarely, if ever, that a judicious selection of food materials receives attention. It is usually a question of individual taste so far as the means at hand will permit, with a complete ignorance of any principles of economy or health. In these directions and others of no less importance there are great opportunities in the domain of sanitary chemistry to render inestimable benefits to humanity.

What has been said of sanitary chemistry applies with equal force to medical chemistry, to agricultural chemistry, and to other special fields. But I feel sure that the details of the methods of instruction, as well as a consideration of methods based on other recent discoveries, such as the use of models in teaching structural chemistry, can best form a part of the general discussion by teachers who are especially occupied in those particular fields. Perhaps, also, the great border land between chemistry and physics, or chemical physics, should receive attention from those whose investigations are extending our conceptions of the fundamental principles of chemistry.


If I have presented this subject more especially from the standpoint of the preparation for professional occupation, it is because this seems to be the principal demand for instruction in chemistry beyond the elementary branches. But if the value of training in chemistry as a factor in liberal education has not been set forth with due prominence, it should receive just consideration in the discussion which follows. I have not attempted in this paper to include methods or conditions outside of our own institutions. Yet we can not fail to derive great benefit in extending our knowledge of the methods in other institutions through the eminent professors with whom it is our good fortune to meet.

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### PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLS.

*Ore Separators, Etc.*—503,454, August 15, Dilworth, R., ore separator. 503,687, August 22, Seymour, C. E., ore concentrator. 503,034, August 8, Brierly, C. B., ore amalgamator. 503,504, August 15, Straker, S., pulverizing apparatus. 503,765, August 22, Johnson, J. S., amalgamator.



502,663, August 1, Eldridge, G. M., washer and concentrator. 503,023, August 8, Willsie, C. F., separator. 504,240, August 29, Patterson, G. H., dry mineral separator. 504,200-201, August 29, Conklin, G., magnetic concentrator. 503,839, August 22, Fauvel, C. J., method for refractory ores; the falling stream of finely divided ore is oxidized and desulphurized by the action of pure hot air and steam passing in the opposite direction, the incandescent particles of ore then being suddenly quenched in cold water. 502,431, August 1, Eames, H. H., desulphurizing metallic ores; the ores are mixed with carbon and lime, heated in a closed vessel, and subjected to the action of the electric current.

*Gold and Silver.*—502,902, August 8, Evans, G. R., amalgamation of precious metals; a composition of soda, lime, and an oleaginous substance is added to the pulp and mercury in the pans. 504,109, August 29, Macay, J. F. N., extraction of silver from ores; treat ores with cupric chloride, eighty-six parts, and sodium chloride, 424 parts, to one part native silver or silver sulphide. 503,358, August 15, St. Cyr, T. Z. H., composition of matter for coating with silver, containing silver cyanide, potassium cyanide, and water, a solution containing from  $\frac{1}{11}$  to  $\frac{1}{18}$  total weight of silver.

*Iron and Steel.*—504,282-308, August 29, Shaw, S., a cupola furnace for melting iron. 502,492, August 1, Höfer, H., refining iron; the liquid metal is conducted through a zigzag channel and reducing gases are passed through the channel in the opposite direction. 502,482, August 1, Dauber, A., process of making iron; ore and flux without carbon are charged into the furnace, a gas containing oxygen is introduced at the zone of preparation, carbon, super-heated steam, and hot air are introduced at the zone of carburization, carbon, super-heated steam, air, and a heated combustible gas at the zone of melting, and into the crucible containing molten metal, a mixture of gas, super-heated steam, and air. 503,423, August 15, Kidwell, J. W., glazed iron; due to titanium. 503,816, August 22, Walrand, C., and Legenisel, E., process of manufacturing steel.

*Zinc.*—502,822, August 8, Lewis, G. T., impure zinc oxide is treated with water and a caustic alkali, sulphur salts of zinc are dissolved, and zinc oxide is precipitated.

*Tin.*—504,238, August 29, Owen, D., apparatus for purifying molten tin.

*Aluminum.*—503,070, August 8, Broadwell, E. C., coating with the metal. 503,900, August 22, Case, W. E., manufacture of aluminum fluo-sulphate. 503,901, Aug. 22, Case, W. E., aluminum compound. 503,929, Aug. 22, Hall, J. B., electrolytic method for aluminum; the current is passed through a fused bath of aluminum, sodium, and lithium chlorides.

*Acids.*—503,847, August 22, Hacker, F. B., and Johnson, A. C., sulphuric acid apparatus. 503,286, August 15, Luhmann, E., carbonic acid manufacture. 503,557, August 15, Solvay, F., apparatus for distillation of hydrochloric acid. 504,264, August 29, Bergmann, F. J., wood-

vinegar manufacture. 502,424, August 1, Precht, H., meta or pyrophosphoric acid combinations are obtained from phosphates of the alkali metals by melting the insoluble salts with a salt of the alkali metals and rapidly cooling to prevent crystallization.

*Water.*—503,140, August 15, Hoppes, J. J., apparatus for purifying water. 502,408-409, August 1, Thomas, J. E., and Grow, E. P., aerating distilled water.

*Brewing and Distilling.*—504,074, August 29, Bradley, E., and Dickerson, E. N., increasing yield of alcohol from alcoholic distilled liquors. 504,145, August 29, Zwietusch, O., beer manufacture. 503,168, August 15, Schneider, G. H., brewing beer.

*Tanning and Dyeing.*—503,235, August 15, Grognet, F., a composition of clay, talc, and barium oxide for preparing hides. 503,987, August 29, Ruemelin, G., tanning; cleaning hide with Glauber's salt, then with a solution of ammonia and grease or oil. 504,012-013-014, August 29, Zahn, W., tawing hides or skins; chrome-alum, zinc sulphate, sodium chloride, potassium sulphide, manganese sulphate are used, and the reduction of chromium acid compounds by arsenite salts is covered by 504,013. 503,148, August 15, Lauch, R., substantive brown dye. 502,912, August 8, Poirrier, A. F., and Rosenstiehl, D. A., black azo dye. 502,765, August 8, Schmidt, R. E., blue alizarin dye. 502,603, August 1, Bohn, R., green-blue alizarin dye. 503,305, August 15, Bender, F., orange dye; derived from acridin. 502,368, August 1, Lauch, R., and Krekeler, C., black azo dye. 502,369, August 1, same patentees, reddish blue azo dye. 503,237, August 15, Heftler, M., and Benard, G., apparatus for extracting dyes, tanning liquors, etc., from stock containing them.

*Organic Compounds.*—502,504, August 1, Thoms, H., para-phenetol carbanide. 503,748, August 22, Lederer, L., amido-crotonyl-anilid,  $C_{10}H_{10}(NH_2)NO$ . 503,295, August 15, Schmidt, R. E., hexaoxyanthraquinone and process for making it. 503,066, August 8, Thoms, H., salicylate of para tolyldimethyl-pyrazolon. 503,743, August 22, Geronmont, F., lactyl-paraphenetidid. 503,401-402, August 15, Borgmeyer, C. L., pyroxylin solvent and its compounds; the former is an ethyl alcoholic solution of oil of caraway chaff; the second substitutes oil of clovebuds for the oil of caraway. 502,546, August 1, Borgmeyer, C. L., pyroxylin solution; effected by dissolving pyroxylin in oil of lemon grass. 502,547, August 1, same party, pyroxylin dissolved in amyl alcohol solution of oil of cedar leaf. 502,921, August 8, Borgmeyer, C. L., pyroxylin solvent; oil of cassia, artificial or synthetical.

*Paints and Varnishes.*—504,064, August 29, Field, W. D., varnish. 504,211, August 29, Gallinowsky, ship's paint; hydro-magnesite, quick-silver chloride, and metallic oxide are given as the ingredients. 503,424, August 15, Kidwell, J. W., pigment or paint; contains oxide of titanium and asphalt.

*Plasters, etc.*—503,592, August 22, Flynn, J., composition for plaster;

"sand or marble dust, gypsum, slaked lime, talc, mineral pulp, potassium carbonate and glue absorbed in quick-lime." 503,425, August 15, Kidwell, J. W., non-corrodible plastic composition for building blocks, titanic materials, and asphalt. 503,336, August 15, Turnbull, G. A., composition of matter for roofing; contains "gypsum, plaster of Paris, powdered salt and flowers of sulphur."

*Miscellaneous.*—503,583-584-585-586-587, August 22, Dupont, F. G., and P. S., smokeless explosives. 502,416-417, August 1, Groat, E., apparatus for reducing and softening bituminous rock. 503,028, August 8, Archbold, G., extracting hydrocarbons from bituminous rock; subjecting rock to sulphurous acid. 503,556-558, August 15, Solvay, E., treatment of pulverulent materials. 503,451, August 15, Case, W. E., apparatus for electrolysis of fused salts. 502,360, August 1, Holland, E. K., regenerative salt furnace. 502,642, August 1, Tatham, E., illuminating gas; contains pure oxygen and a heavy carbonaceous gas. 503,612, August 22, Meitzler, G. R., silver cleaning and polishing composition; "whiting, powdered soap bark, oil of sassafras and carmine" are claimed. 504,105, August 29, Corleis, E., and Reinsch, H., carbon rods for electric arc lamps; carbon impregnated with tungstic acid or a salt of the acid. 504,199, August 29, Cheever, J. D., preserving fibrous materials; a solution of catechu, potassium bichromate, and creosote are used. 502,867, August 8, Schöler, L., fire-proofing composition; ammonium phosphate and ammonium sulphate are given. 502,964, August 8, Habedank, C. F., composition for lithographic transfers; "water, partly neutralized nitric acid, and tannic acid." 503,801, August 22, Mills, J. E., composition for tempering; "oak ashes, water, tallow, slaked lime, salt, ground horn, and potassium cyanide."

## NEW BOOKS.

REACTIONS. A SELECTION OF ORGANIC CHEMICAL PREPARATIONS IMPORTANT TO PHARMACY IN REGARD TO THEIR BEHAVIOR TO COMMONLY USED REAGENTS. BY F. A. FLÜCKIGER, PH.D., M.D. Translated, revised, and enlarged by J. B. Nagelvoort, analytical chemist to the Pharm. Chem. Laboratory of Parke, Davis & Co. Authorized English edition. Detroit, Mich., U. S. A. George A. Davis. 1893. pp. x + 154.

This work aims to give the physical properties and principal reactions of the more important organic chemical preparations used in medicine. The book opens with a numbered list of the reagents most commonly used and their preparation, and then follow 109 pharmaceutical products alphabetically arranged, with from one to ten reactions under each. Rather more than one-half the compounds treated of are alkaloids, among which

those of opium and the cinchona bark occupy a prominent place; nearly one-third are synthetic products introduced into pharmacy within the last few years. The compounds are well selected and the various reactions are fully and minutely described. As far as the scope of the book goes, the work is excellently and accurately done, and this is especially the case with the opium and cinchona alkaloids. Very few errors mar the book, and these few are evidently typographical, as " $C_6H_5(CH_3)$ " for  $C_6H_5(CH_3)_2N_2O_2$ , as the formula of theobromin (p. 145); "mercurous nitrate, (Millon's reagent)," p. 25,—Millon's reagent is mercuric nitrate, and the reaction given for brucin is very different from that originally described by Flückiger with mercurous nitrate.

The book, however, would have had a more practical value if its scope had not been confined so closely to the narrow limits of identity reactions. Differential reactions are indicated only by reference, and in the case of almost two-thirds the compounds not a single differential reaction is pointed out. A synoptical table of the principal reactions studied would have greatly enhanced the value of the book. Further, it is stated in the preface that the "reactions \* \* \* are not to be relied upon where impurities of any kind are likewise to be considered." The chemist does not, however, always meet with pure substances, and while in a few instances methods of purification and of identification in the presence of impurities are given, these might with value have been multiplied. The reagents are generally designated merely by a number ("Reagents 6, 12, 13, 14, 16, and 24 give precipitates," p. 72, etc.), referring to the table at the opening of the book; this saves space, but its advisability from a chemical standpoint is questionable.

The translator's additions are valuable and the translation is generally well made, though in a few instances obscure (cocain, last sentence), or too literal ("amorph powder," p. 39; "the slowly colored in the cold \* \* \* fluids," p. 51). The spelling laid down in the rules of the A. A. A. S. is used, and the book is neatly printed on fine paper, with wide margins for notes.

J. L. H.

A GUIDE TO STEREOCHEMISTRY. ARNOLD EILOART. 96 pp. Price, \$1.00. New York. Alexander Wilson. 1893.

In this book by Dr. Eiloart the endeavor is made to summarize the mass of speculation which has been published of late concerning the stereochemistry of carbon and nitrogen compounds. Although the volume is designed to serve as a text book the author's treatment is largely confined to recent speculative work, and it gives undue prominence to insignificant and weak points. As a text book planned to give a clear idea of results more generally accepted, the classical little *Stereochimie* of van't Hoff (new edition, 1892) is likely to be of more service. Full half of Dr. Eiloart's book is devoted to an alphabetized list of citations, and to this is appended an illustrated description of wooden models (tetrahedra) designed to represent the structural formulas of organic compounds. J. E. T.

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**Note on the Determination of Phosphorus.**—Mr. Edward K. Landis writes to the editor as follows: "I have been using for nearly a year a ground glass funnel for phosphorus after Dudley's method and find that the paper sticks tightly to the glass, permitting the upper edge to be thoroughly washed, and thus avoiding a source of error mentioned by Dudley in 'Discrepancy in Chemical Analysis.' This may prove useful to others."

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**ERRATUM.**

In the July number, page 385, eighteenth line from the top, "(and methyl orange)" should read "(and not methyl orange.)"

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### THE EDUCATION OF INDUSTRIAL CHEMISTS.<sup>1</sup>

BY GEORGE LUNGE, PROFESSOR OF TECHNOLOGICAL CHEMISTRY AT THE FEDERAL  
POLYTECHNIC SCHOOLS, ZURICH.


THE vast domain of chemistry is now divided into a number of fields, worked by different men, and according to methods differing widely from each other. It has not always been so. Berzelius, Dumas, Liebig, and some of the minor stars shining at the same time as these great luminaries, combined the mastery and leadership in inorganic and organic chemistry as a pure science, with applied chemistry in all its branches. In no case, perhaps, has this widely embracing spirit been more clearly exhibited than in that of Liebig. I will not dwell for a moment upon his immortal achievements in pure chemistry; these are, after all, the central tower of the vast building which he has reared, and they form the foremost title to his being classed as the greatest of all the chemical giants our century has produced. But hardly, if at all, inferior to this are his achievements in applied chemistry. Need I remind my hearers where Liebig found those two immensely important fields, agricultural and physiological chemistry, and where he left them? His merits with respect of industrial chemistry are perhaps less generally known and appreciated, but they are also sufficient to warrant the assertion that during the first half of this century no teacher of chemistry, except, perhaps Dumas, occupied so high a place in technical matters, and was more

<sup>1</sup> Read before the World's Congress of Chemists, August 26, 1893.



frequently appealed to for assistance and enlightenment by chemical manufacturers than Liebig. It was probably not a mere accident that one of the very first men who occupied a chair entirely devoted to technological chemistry in its stricter sense, Friedrich Knapp, was Liebig's brother-in-law. It will not be disputed that the teachers of industrial chemistry of this day, if they look for their spiritual ancestors of half a century ago, can find hardly any men of mark who were at that time mere specialists in technology, but they must and can lay claim to being the humble successors of those grand heroes of pure science of whom I have spoken at the outset, and who have combined excellence in theoretical and in applied chemistry.


It is very different to-day. Hardly one of the men whom we are now proud of revering as our leaders in pure science, is intimately connected with industrial chemistry. The last of the great men of whom that could have been said, August Wilhelm Hofmann, has passed away from us; and he had about thirty years ago ceased to be productive in that specialty. Of course, a good many other first-class theoretical chemists have some connection with industrial pursuits; some of them have even taken out patents, and devote part of their time to the "business" element of applied chemistry. But no one of them occupies himself with teaching industrial chemistry, or working, or writing in that field; and few of them have any extended knowledge or interest in that domain. Industrial chemistry in that respect is exactly on the same ground as pharmaceutical, or agricultural, or physiological chemistry. All of them have branched out too far and have become too closely intertwined with other sciences to be embraced by the same men whose life-work lies in pure chemistry; all the less as the latter have been compelled long ago to parcel up their own field among various workers. It is now quite an exception for the same man to pursue more than one of these three directions: General and physical, inorganic and analytical, and organic chemistry. Nay, the time seems near at hand when the organic chemists will be divided into fatty, aromatic, and pyridine chemists, and perhaps some further shades. It is, of course, indispensable for every chemist to be acquainted with all the branches of his profession, and for the



elementary grades even the teaching of those various branches may be and generally is still left in a single hand. But the creative work is now distributed among quite a number of classes of chemists ; and in the highest grades the teaching must be similarly divided among specialists. Thus at the Zurich Polytechnic School there are four full professors for the various departments of pure and applied chemistry, with four assistant professors, and a fifth chair has just been founded.

Since industrial chemistry has become an entirely distinct department of science, and since the instruction therein has naturally been entrusted to separate teachers, it is important, both to those who intend to study industrial chemistry as a profession, and to those who have to employ the men educated for that pursuit, that it should be taught in the best possible manner. This is so self-evident that it sounds almost like a commonplace to speak of it ; and yet it is far more difficult than it looks. Whilst the teaching of pure chemistry is carried on very much the same lines all over the world, it is certainly not a settled question how chemical technology is to be taught, and great differences of opinion exist in that respect, among the leaders in that branch of science, the governing boards of technical schools, and the practical manufacturers who look for the best possible preparation of their employees.

A few years ago public discussions on the best way of educating young men for the profession of technical chemists took place very extensively, both in Germany and England. The societies of chemical industry in both countries, a number of private gentlemen, and in Prussia even the State Department of Education took part in those discussions. I myself have borne a good share in them, and whilst standing up for what both experience and common sense induced me to maintain, I have given due weight to the arguments brought forward from other sides. I have also had a good opportunity of carrying out at least a good portion of those views which I then felt bound to take, in one of the most flourishing centers of technical instruction. As far as I can judge, only a faint echo of those discussions has reached the country in which I have now the honor of speaking. But it cannot be indifferent to this great nation



Now the things men are to be fitted out for carrying on the pursuit of technical chemistry. Indeed, metallurgy, assuredly one of the greatest American industries, is nothing but a special case of technical chemistry, and any remarks made upon the latter apply to a great extent also to the former: but my theme is to urge to take notice of the special requirements for the instruction in metallurgy to-day.

I hope, therefore, to be excused, if I touch briefly on the main points of these discussions on the education of technical chemists, so far as they may seem to possess interest for this country. I shall confine my remarks exclusively to the highest class of teaching, such as is practised at universities and polytechnic schools; both because time would not permit me to discuss the lower grade schools as well, most useful though these are in their way, and because I do not possess the necessary personal experience and competence for dealing with that part of the subject.

Before entering upon the course of instruction to be followed at the colleges themselves, we must necessarily look to the foundation of that edifice; that is the previous training of the young men who are to enter a college of which technical chemistry forms one of the principal branches. I am not sufficiently acquainted with the various classes of schools existing in this country to tread upon this ground; but so many of my hearers have been in Europe, or at least know European institutions, that I may take it for granted that I shall be understood when speaking of the various systems prevailing in Europe. I shall venture even further, by speaking chiefly of the German and Swiss schools, which are generally acknowledged as being among the best of their kind.

In these countries two systems of education are found side by side, and often in tacit or outspoken opposition to each other, viz., the classical or humanistic, and the modern or realistic system. The former, as embodied by the German gymnasien, the English grammar schools, and the French Lycées, builds up the whole of education on the foundation of Latin and Greek, devoting but little time to modern languages, including the mother tongue, about as much to mathematics, and very little

indeed to natural sciences. Youths brought up under this system have very frequently turned out splendid men in all walks of life, and many savants of the first order have sprung from such classical schools. The devotees of this system are not tired of repeating, with that dogmatic tone fostered by itself, that higher mental culture cannot be brought about by any other means. A man, they say, who knows Latin and Greek, or who at least has known something of these languages at a former period of his life, has thereby trained his mind in such a wise that it is open to receive knowledge of all kinds, whether philological, or historical, or mathematical, or belonging to the realm of natural science. But they go much further; they boldly say that nothing but this classical training enables a man to thoroughly grasp even the inductive sciences in their highest ramifications. Others may grub about in the lower regions; they may do useful work in chemical analysis, in collecting plants or beetles, or stones, and the like; but the fundamental discoveries, the grand generalizations, all the higher attainments in science are reserved for those who have drunk from the fountain of classical studies. Nor are the men who speak in this way shaken in their belief, which with them amounts to a dogma, by the hard fact that many men of the highest order, of whom I will only mention Faraday and Liebig, do not conform to the rule of the exclusively saving power of classical education.

In this practical country such views are probably very rarely met with, and many of my hearers may think that any discussion about them is like fighting with shadows. But in Europe, at all events, they are realities. Men like Hofmann and Dubois Reymond (of whom the second later on withdrew from that position) have pronounced in their favor, and probably the majority of German university professors still adhere to them, more or less outspokenly. Up to this moment in Germany the majority of those entering college for the purpose of devoting themselves to the study of pure science, and all those who enter for medicine, come from the classical gymnasien, where Latin and Greek are the central pillars of education; even for the polytechnic schools the classical gymnasien enjoy the same privileges as the realschulen, where only Latin or no classical language at all is

taught, but in lieu of that far more of modern languages, of mathematics, chemistry, physics, drawing and so forth. It will be perceived from this that in Europe it is not yet a waste of time and energy to stand up publicly for the conviction that the classical languages, so far from being helpful in the pursuit of scientific and especially technical studies, are most decidedly *injurious* to it, both directly and indirectly, by blocking the way for other matters of far greater importance. I speak feelingly on this point, for I received a thorough Latin and Greek education, and my original intention was to devote myself to the study of the science of language. I cannot, therefore, be upbraided with talking about matters of which I know as much as a blind man of colors, when discoursing on the value of a training in the classical languages, which I have loved dearly, and in which I have worked with far more than the ordinary zeal of a collegian. But I am bound to say, as a chemist, that I have bought my whistle far to dear. It would not be becoming, if I went any further into personal matters, but thousands are in my position, and most of them will, like myself, say that, if we have done our little share in some theoretical or practical branch of natural science, it has most assuredly not been in consequence, but in spite of our classical training, which taught us to esteem words more highly than things, and book-learning as the only kind of knowledge worthy of a noble and really cultivated mind.

I have come to the conclusion that, taking men as they are, and looking at the fact that only a small minority are able to give an unlimited amount of time to their preparation for practical life, those who intend to embark in the career of natural science, in medicine, or in any technical line, ought to content themselves with only *one* classical language, that is practically with Latin, although some well-meaning enthusiasts would in this case plead for Greek. In my opinion a man may get on perfectly well in every one of the branches named before without knowing even Latin, and I make bold to say, he may also acquire a mental education as deep and real as that generally approached through the classical languages; but in Europe, at all events for the present generation, a knowledge of Latin is still desirable for those who move in the higher spheres of

society, whilst it is the merest sham to pretend that there exists in those circles, with trifling exceptions, more than a faint remembrance of the Greek with which they painfully struggled in their earlier years. The whole of the time given to Greek, and a good deal of that spent on Latin in the gymnasien, is in the realschulen devoted to modern languages, to mathematics, to natural science and to drawing, which subjects in my firm belief are not merely more useful for all practical purposes, but which form the youthful mind in a far healthier mould than the one-sided pursuit of classical studies.

I am afraid I have, after all, dwelt too long on the chapter of preparatory education, as I am speaking in a country where the immense prestige enjoyed by the classical languages in the greater part of Europe does not exist, and where the opinions which I have stood up for are taken for granted without any discussion. Let us, therefore, now enter upon our proper field, the special studies to be pursued at a university or technical college by those who mean to devote themselves to industrial chemistry.

It will be granted on all sides that at this time of day no technical chemist is worthy of that name who does not possess a sound and thorough knowledge of general chemistry. The time is past when the rule of thumb was paramount; when most factory managers recruited themselves from the ranks of "practical" men, understanding thereby mechanics, manual laborers, or business men, who looked down upon the chemist—if such a person was at all attached to the works—as a testing machine, to be kept in his proper place and to be mistrusted, whenever he ventured for a moment beyond the hole which was by courtesy styled the "laboratory." Nor were these "practical men" altogether wrong in their estimation of the "chemists" they came in contact with; for the majority of those chemists had started as bottle washers to a "chemist" similarly educated, and had at best acquired some smattering of chemistry at a night school or the like. These men were often qualified by natural quickness of intellect or by a practical turn of mind for better things, but science could not lead them on, for of that they were really almost innocent. This sort of works' chemists

lowered the standing of the whole profession. Even many so called "analytical chemists" were only brought up to this profession as apprentices, as to an ordinary handicraft, and these were only a step or two more advanced in science than those who had commenced with the bottle-washing department. This state of things is not so far removed from the present time as some of my hearers may think. Thirty years ago, when I transferred my abode from Germany to England, I found it to a great extent prevailing in the latter country, and it was not altogether unknown in the former. Even then many scientifically educated chemists had been turned out, chiefly by the German laboratories; but they had mostly to accept positions and salaries corresponding to the low estimation in which the profession of chemistry was then held at most chemical works.

The time I mention, saw, however, the commencement of a better era. Just about that epoch the new industry of coal-tar colors, which had commenced with the discovery of Perkin's mauve in 1856, began to assume larger and larger proportions. It had become abundantly clear that that industry could be carried on and extended by none but scientifically trained chemists; more than that, it soon became apparent that an elementary knowledge of chemistry, such as had been thought quite sufficient for practical purposes, would not do here; that chemists were required conversant with every recess of their science, and trained not merely to receive what others had discovered, but to think independently, to strike out new ways, and to enlarge the domain of science. Men really capable of doing this found an abundant field at the color works, and naturally a demand for good chemists sprung up which was soon overtaken by the unremitting supply flowing from about thirty German and Swiss universities and polytechnic schools. The men who could not find places in the coal tar industry overflowed into other domains of manufacturing chemistry, and soon enough it was found that the men of that stamp were after all far more valuable than the old "testing slaves," as they were sometimes ironically called. The operations of manufacturing chemistry in most of its branches assumed quite a different face under the light shed upon them by science, which transformed them from a string of

merely empirical rules into a carefully elaborated and constantly checked system. The difference, both in the quality of the articles and the quantitative yields between our time and thirty years ago, is simply marvellous in many branches of manufacturing chemistry, and nobody dreams of denying that this has been brought about by the firm hold science has now got over that industry.

There is no more need of preaching nowadays that a devotee of technical chemistry must be a good scientific chemist to begin with. True, not every student needs or will penetrate to the more profound depths of science; but so much is universally granted that during his college career he must enjoy the fullest opportunity for this, and that consequently not merely the universities, but the polytechnic schools, and other institutions of the same character, as they exist in this country under various names, must be furnished with first-class teachers and first-class laboratories for general chemistry. Nor can there be the slightest doubt that a good knowledge of physics, mathematics, mineralogy, and geology should be acquired by a technical chemist, not, of course, to the same extent as chemistry itself, but still in a sound manner, not as amateur work. The biological disciplines will never be wanting at such institutions, and a knowledge of them is certainly useful and becoming for every educated man, let alone a man of science, but it would be an exaggeration to say that they are indispensable to a technical chemist as such, and they are often entirely left out in his curriculum.

Strange to say, here many students and even many institutions stop. The young men leave college, well grounded in chemistry and the allied sciences, but entirely or at least almost entirely ignorant of technology, of mechanical engineering, and of mechanical drawing. This is the case at all German and at most other universities, from which we must here carefully separate the polytechnic schools, and at a number of special colleges of chemistry. Although at some of these institutions some little time is given to technology, it is so little that the results of teaching it are almost nil.

What that means, nobody knows better than I. My college




studies fell in a time when the polytechnic schools were still comparatively in their infancy, and although I had from the first intended to devote myself to industrial chemistry, I thought it most natural for that purpose, when I had finished the gymnasium in 1856, to go to a university, from which I came away without any knowledge of mechanical drawing, of engineering, or of chemical technology, apart from some meager allusions to it in the general chemical lectures. Even now, more than thirty-seven years after that time, hundreds of young men enter upon the same career in the same way. Those of them who either turn over to pure chemistry (whose number must always be very small) or who are lucky enough to find entrance in the scientific laboratory of a color works, or else who are content to be confined for ever in the laboratory of another kind of chemical works, without a chance of rising to the management, will have done quite right in having carried on their studies at a university. But those who ever mean to rise to the position of superintendent, and to get to practical manufacturing work as soon as possible, will meet with the same difficulties I did. They will soon become conscious of their utter ignorance of the means by which manufacturing processes are carried out on the large scale; they will be constantly put to shame by men or even youths of infinitely less learning, but familiar with the working process; they will commit blunder after blunder when left to themselves, and still worse ones when they try to realize improvements which they have conceived, and which may possibly be quite right in principle; they will not even be able to express what they want to an engineer or furnace builder, since they cannot make or even properly understand technical drawings. Some men, when thus thrown upon their own resources, by dint of natural ability and by long and painful labor, get the better of all these drawbacks; but many others do not succeed in their endeavors, and they have either to pass over to some other career or else they remain locked up in inferior places, no better than those of the "testing slaves" I have spoken of.

Far better on the whole is the lot of those young men who have acquired a knowledge of technology and engineering. It takes them much less time to be at home in any factory where


they may have found a position. No previous teaching at any technical school can get them far enough to enable them to instantly take the manufacture in hand and carry it on like those who are accustomed to do so. But they have been taught to *think* and to *see* matters in a technical light; they know where to look for important points essential to the success of operations on a large scale, and they know how to translate any ideas of theirs into reality by such means as are suitable for factory operations. They will, of course, not be entirely exempt from mistakes; but their blunders will hardly ever be so gross as those of their colleagues who have received an exclusively scientific teaching.

A training of the kind just sketched is not, and cannot be given at an ordinary university, but only at institutions set apart for that purpose, such as the polytechnic schools, in Europe, and the various institutes of technology existing in this country. Strange to say, the hitherto greatest of all industrial nations, England, is altogether devoid of efficient institutes of the kind; and although for many years past this deficiency has been clearly recognized, although the undeniable comparative decline of some important branches of industry, in England, has been traced to this cause, and although there has been no lack of royal or municipal commissions, of public discussions, and even of large expenditure for remedying this state of things, very little has been effected in that direction. Unfortunately for England, her splendid achievements in all realms of mind and matter have created there a feeling of innate superiority over all other nations of the world, more quiet than the loud self-assertion of the French as the "*grande nation*," which professes to march in the van of civilization, but perhaps even more deep-seated and resolute. This feeling produces a strong undercurrent in English thought which has hitherto paralyzed all useful action in the quarter I am speaking of. The majority of those who have ultimately to decide on matters of technical education have the quiet conviction that, in spite of all the lamentations about the decline of commerce and the uprising of other nations in industrial matters, it is quite sufficient to trust to English commonsense, pluck, and perseverance, which with certainty will tide the



country over any temporary reverses, and triumph over all these foreign shams.

Nobody can have greater admiration for the sterling qualities of the English character than myself. I have spent a dozen of the best years of a man's life in England. I have become a loyal British citizen, and an English author. But it is precisely my sympathy for my adopted second fatherland which makes me mourn that fatal blindness to the defects of English technical education prevailing in that country. I will not speak of the object lessons which this country is daily giving to England, for instance of the fact that the production of that specially British article, iron, is now considerably greater in the United States than in Great Britain, that coal will soon follow suit, and that American machinery of many descriptions has asserted its superiority over English machinery in many important cases. All this is well known and is, however reluctantly, conceded in England; but the English people comfort themselves to some extent with the idea that America, on the one hand, enjoys immense natural riches and facilities accounting for her most signal industrial triumphs, and that, on the other hand, the Americans are Anglo-Saxons like themselves, flesh of their flesh and blood of their blood. It is surely unnecessary to point out the fallacy of the latter argument in a city where born Americans form only a fifth or a sixth of the population, and only a minority of those born Americans are of purely Anglo-Saxon descent. It is very often forgotten on the other side of the ocean that community of language is something very different from identity of race, and just in commercial and industrial matters both the good and the less favorable features of the American and those of the English character are very different. But it is unnecessary to pursue this side of the question any further. Those Englishmen who hold to the firm belief in the innate industrial, colonizing, political, and even physical superiority of their race over all others forget that all this is of very recent date. The Anglo-Saxons had conquered Britain more than a thousand years, and the Normans more than five hundred years, before England possessed a mercantile marine or navy to speak of. Four hundred years ago the German Hanse-towns were im-



mensely superior to England as maritime powers, and much more recently this applied to the Dutch. The office of the Hanse-towns, in London, was called the *Stahlhof*, because in the middle ages no iron or steel was made in England, and the importation of those articles from Germany formed a very important branch of trade. The blast furnace and the cementation of steel have been brought into England from Westphalia, the textile industries from the Netherlands. It is barely 150 years since England has taken the lead in these industries. How can Englishmen be blind to the thought that that lead may pass away from them, unless they make the same efforts as other nations to keep abreast with all advances of science?


Allow me to give you a very striking example of the novelty of English superiority in the field which is most familiar both to my hearers and to myself; I mean the alkali trade. The name *Leblanc* at once recalls the fact that the manufacture of soda from common salt was invented in France, but few Englishmen will realize the further fact that it took thirty-five years before England entered the race in this field, while numerous alkali works had been erected in France and elsewhere in the mean time. It is true that in England the alkali manufacture was impossible, so long as an enormous duty weighed upon the salt; it is equally true that immediately after this incubus had been removed, the alkali manufacture sprang up in Great Britain, and in a very short time left all other countries far behind in that line; it is true that this was not merely due to favorable external circumstances, such as the cheapness of salt and coal, and the easy communication with the sea, but perhaps quite as much to the long string of English inventions which have made the English methods of alkali manufacture the pattern from which all other nations have immensely profited. Nobody will more heartily acknowledge than I how much honor and gratitude the whole world owes in that respect to British inventive genius and British enterprise. But that cannot obliterate the fact that, on the one hand, the first British alkali works is less than seventy years old, and that, on the other hand, new methods have already partly superseded those worked out in England, and partly threaten to do so even more in the

future. We behold here a strange turn of the wheel of fortune. The invention of a Frenchman, Leblanc, has laid the foundation of England's greatness in the alkali trade; but an English invention, the ammonia soda process, could not be worked out into a practical process in that country, in spite of many endeavors, and it was left to a Belgian, Solvay, to do this, and to reintroduce the process into England, where it is now carried on according to Solvay's method. It is notorious that the English alkali trade is no longer rapidly expanding, while that of the other industrial nations has made enormous strides. Customs' duties and other external circumstances partly account for this; but a very important part is also played by the more careful scientific training of the managers and chemists in the other countries, exceptions on both sides, of course, notwithstanding.


How the Germans have wrested the most brilliant of all chemical industries, that of the coal tar colors, out of the hands of the English, in whose country the first discovery of these colors was made, and which had to supply all the raw materials for them, is an often told story, which I need not repeat here.

All this (I could give many more examples of the same class) further confirms my opinion that no nation, whether the American, or the English, or any other, has a right to boast of being forever in the van, and to look down upon other nations as innately inferior to itself. Natural advantages of situation, mineral wealth, inventive genius, accumulated capital, an enterprising spirit, are all enormously important factors in creating and extending industries, but they are not omnipotent, not even if all combined; the victory over all these accidental or inarticulate forces will ultimately fall to the scientifically trained human mind; just as the engineer in charge of a large steamer holds in subordination not merely all the brute powers of fuel, furnaces, and machinery, but also a large number of human beings, immensely superior to him in bodily strength, but inferior in knowledge.

Well, how is a first-class engineer brought up? Merely on a knowledge of the physical and mathematical theorems concerning the action of steam and the laws of motion? Certainly not. Nobody would expect such a man to be able either to



build or to work an engine. He must be brought face to face with the hard facts of reality; he must know all about casting, forging, and other ways of shaping metal; he must know a great number of practical points indispensable for designing machinery, and too many other matters to enumerate here. And it is just the same with a manufacturing chemist. If he enters practical life, trusting merely to theoretical knowledge, and to such practice as he has gained with glass, porcelain, and platinum vessels in a laboratory, he is at first as helpless as a child, and he must begin at the beginning, picking up what he can on his way. Some people manage to do this very fast, and it is just to this "practical sense" that the English system of education leaves the students of chemistry; but, I say it with the fullest conviction, it is decidedly wrong there. The time is past when the crudest of all machinery would do for chemical purposes, and when chemists could try to translate their laboratory operations into manufacturing work by merely magnifying the apparatus and substituting one material for another, in which attempt they only too frequently broke down. All this has become the subject of special studies. A manufacturing chemist of first-class standing must nowadays know almost as much about the strength of materials as an engineer, and he must add to this a knowledge of the behavior of all sorts of metals, stone, earthenware, wood, of various coatings, of joints made in different ways and so forth, against the action of ever so many chemicals under varying conditions of concentration, temperature, and pressure. He must know how to produce heat, and in many cases cold, to the necessary degree in the most efficient and economical way. The construction of furnaces of all kinds belongs to his special domain. He must know how to design large vessels of various materials, both open and closed, with or without agitating machinery adapted to special requirements. He must employ presses, pumps, drying apparatus, having regard to what will answer not merely in the engineer's workshop, but under the special conditions of chemical attack and of high temperatures. The arts of disintegration, evaporation, filtering, distilling, fusing, the action of gases upon liquids and solids, the heating under pressure and other operations con-



stantly carried on in chemical works have been so thoroughly developed as to amount almost to special sciences. One of the most distinguished men in the domain of chemical technology, who at the same time would have done honor to any chair of pure organic chemistry, and who more than any other living technical chemist represents the theoretical element in technology, Heinrich Caro, formerly director of the Badische Anilin und Sodafabrik, in Ludwigshafen, in a lecture delivered last year before the Berlin Chemical Society, distinctly declares that chemists for the actual work in a chemical factory (Betriebs Chemiker) cannot receive their training for the above requirements at the Universities, but only at the polytechnic schools, and this judgment has all the greater weight, as Dr. Caro was formerly of the opposite opinion, *viz.*, that at least at such large works as theirs it was best for the chemists to receive a purely scientific training, leaving the constructing work to the engineers appointed at the same works, an opinion which he has seen reason to change after prolonged experience with a large number of chemists from both universities and polytechnic schools.

Nobody indeed who looks at the present state of chemical industry with an unprejudiced eye can deny that a mere training in theoretical chemistry is as unable to cope with the competition to be met with in the rest of the world, as is the formerly universal rule-of-thumb management. We must needs teach our future chemical manufacturers how chemical operations are and ought to be carried out on the large scale. To accomplish this, we must approach the subject from various sides. We must in the first instance teach our students at least the elements of mechanical engineering, of building construction, and of furnace building. This supposes a much better knowledge of mathematics than chemists formerly used to possess, as well as some practice in mechanical drawing. We must further introduce them to a description of the various classes of work they meet with in their career. This should be done in different ways. At all events the leading chemical industries ought to be described, going into all essential details of apparatus, and thus serving the double purpose of a preparation for those in-

tending to enter that special field, and of giving to all others important suggestions how the appliances invented for one manufacture may be used in another, possibly entirely different from the first. Many of my former students who are now employed in the industry of coal-tar colors, or in dyeing and tissue printing, have told me how useful to them has been the description which they received as students of the apparatus employed in the manufacture of heavy chemicals. The reverse is just as possible, and actually met with. Thus thirty or even twenty years ago the use of centrifugal machines and filter presses was almost unknown in the alkali and chlorine manufacture; nowadays it is quite common. For another very practical reason it is necessary to offer at a technical college instruction in all the more important branches of technical chemistry, *viz.*, because such a college should enable all its students to take situations wherever they find them open. This applies to the great majority of students, although there is always a number who go to college with a specific purpose, principally those connected with manufacturers whose works they are destined to enter after finishing their studies. I cannot therefore approve of the plan proposed by an Austrian professor, according to which each polytechnicum is to cultivate a separate specialty—say sugar making, or brewing, or alkali making, or dyeing, or color making, and so forth—with the idea that a youth of eighteen years, before entering on his academical career, should absolutely fix what special manufacture he is to devote himself to afterwards. Suppose he has studied four years with the entire object of becoming a sugar manufacturer, but at the end of that time it is seen that that trade is declining, or has migrated elsewhere, or that the supply of sugar chemists is largely in excess of the demand. What can he then do but throw up all he has studied and begin over again on a different line? If he has prepared himself less specially, but more universally, he will probably not be quite so useful at a sugar works for the first few months, but he has the chance of taking to any other manufacture where there is a vacancy, and to pick up whatever situation comes in his way.

I certainly cannot approve of the other extreme, introduced at the Ecole Centrale in Paris, where all the students, whether



they mean to follow the profession of civil engineering, of mechanical engineering, or of industrial chemistry, are taught exactly in the same way and receive instruction both in mechanical and chemical subjects. I do not know whether that system produces good engineers; but I am told it does not produce good chemists, and I can readily believe it.

I should also like to correct a mistake, not infrequently met with, *viz.*, that the teaching of chemical technology is of comparatively little value, because the professors themselves generally are not acquainted with the very last phases of progress made in the manufactures, seeing that there are constantly new inventions made, many of which are kept secret, or are very imperfectly described by patents. This is perfectly true, and yet it is of very little importance. No teaching of real or imaginary trade secrets would enable a mere book or laboratory student to carry on real work on a large scale; only practice itself can do that. But that practice will be all the more quickly and thoroughly acquired, the more the student has heard of technology generally and of the special branch to which he devotes himself afterwards. Any fresh improvements he finds applied when entering a manufactory will be quickly grasped by one who enters upon his practical work, armed with such general preparation as has been described above, which has taught him to think and see matters in a technical light, as I have expressed it above.

There are some subjects which are common to all chemical operations on a large scale, and which ought to be learned by every student. The technology of water and of fuel are the principal subjects in question, and the latter especially opens out a large field, embracing the construction and working of heating appliances of all kinds. These, together with the elements of engineering and building construction on the one hand, and with the thorough study of theoretical chemistry and the concomitant sciences of mathematics, physics, mineralogy, and geology, and lastly with practice in the chemical and physical laboratory and at the drawing board, ought to fill the first years of the study at a technical college. The last years ought to be devoted to chemical technology proper, and to a special study of

such subjects as have not been sufficiently mastered before, or as are likely to form the main occupation of the student in later life.

The whole study is generally crowned by the obtention of a degree, in Germany either a "diploma," or the title of Ph.D. The latter, owing to the jealousy of the old universities, cannot yet be conferred by the polytechnic schools themselves, but it is very frequently earned by their students afterwards. I have found the greatest possible benefit to arise from this system of "diploma examination." A student, instead of losing himself in a specialty, and being too much absorbed thereby, to the detriment of his general scientific and technical culture, or of falling into habits of laziness and dissipation, or else of becoming an exclusive devotee to athletic sports, is compelled to concentrate his energies once more on all the more important branches of his life-studies, and to carefully rehearse what he has once learned, but much of which he will have forgotten. Taking human and especially youthful nature as it is, there is no denying that mere abstract considerations of what may be good for a man's future are not sufficiently powerful to counteract the forces, both good and bad, which tend to draw a student away from his work, and that it is immensely better to hold out to him an immediate aim to strive for, in healthy competition with his fellow students. The German polytechnics are in this respect less fortunate than our Swiss institute; in the former only a small minority of the students go in for the diploma, whereas with us most of the students enter with the purpose of ultimately obtaining the diploma. Many of them drop off on the way; some others, in spite of all exertions, do not reach the goal, but about half of the total number of students leave the school, not merely in possession of a piece of stamped paper, but in that of all the additional knowledge they have acquired in quest of that paper, and which they would not have got without such an inducement. It is a great satisfaction to our institution that its diploma is eagerly sought, and hard work bestowed upon it, by nearly all the sons of wealthy manufacturers, who have been born with a silver spoon in their mouth, and whose future places are absolutely secure to them without a diploma;

but these young men are well under the sway of that healthy spirit of doing work which prevails at our institution, in consequence of the great value attributed to the diploma. Most of these wealthy young men are ashamed of standing lazily by, while their fellow students strain every nerve for the diploma; they want to show what mettle they are made of, and they therefore go in for the diploma as well, to their lasting benefit in more ways than one.

The diploma examination in our case comprises a full knowledge of general inorganic and organic chemistry, to the same extent as the universities require for the degree of Ph.D., further, of mechanics, physics, and mathematics, including the elements of the calculus, and at least some of the departments of natural history. In the field of chemical technology the general chapters are compulsory, but the candidate has the option of being examined in a number of special chapters according to his choice; further in the elements of engineering and building construction. Moreover, each student must do a considerable amount of special laboratory work extending over a whole semester, by which he proves his skill in all departments of chemical analysis and in preparing any chemical substances described in chemical literature or in patents. For the diploma itself we do not require any difficult research work; but most of our graduates aspire to the title of Ph.D., and for this they are obliged to do substantial research work which generally keeps them in the laboratory about a twelvemonth over and above their proper college time. When they have accomplished this they have not merely got an ornamental title, but they have, what is certainly of greater importance, acquired such a mastery of our science that we can confidently dismiss them into practical life. Even then, it is hardly necessary to say, great differences exist among them. Some remain in modest situations all their lives, but others rise quickly to higher places, every one according to his abilities and to his deserts. The successful men, without a single exception that I know of, look with warm gratitude on the institution where they have received their scientific training and which has raised them above the hap-hazard luck of rule-of-thumb experience as

well as above the one-sidedness of autodidactic studies—both of which are excellent as far as they go and not to be despised by any means in themselves, but neither of which can cope with a carefully devised and conscientiously carried out scheme of training the mind for the profession of a technical chemist such as I have had the honor of laying before you. Nobody is more conscious than I that at no existing institution has the beau ideal of such a scheme as yet been attained, but at Zurich we believe that we are, on the whole, on the right way, and that we shall do well not to exchange our plan for a totally different one, but rather try to improve it on the lines on which we are now working.

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### THE NEED OF STANDARD METHODS FOR THE ANALYSIS OF IRON AND STEEL, WITH SOME PROPOSED STANDARD METHODS.<sup>1</sup>

By C. B. DUDLEY AND F. N. PEASE, CHEMIST, AND ASSISTANT CHEMIST, PENNSYLVANIA  
RAILROAD COMPANY, ALTOONA, PA.

MUCH might be said upon the desirability, nay even necessity of different chemists being able to get concordant or agreeing results, when working in the same field, or upon the same sample. If two chemists happen to be engaged in an investigation, or research in the same field, it is obvious that the value of any conclusions, which they may reach, is very small, if the analyses obtained by each, do not agree within reasonable limits of error. Or again if chemical analyses are to be used as the basis of commercial transactions, and the chemist in the interest of the buyer, does not get the same results as the chemist in the interest of the seller, it is clear that the transaction can only be brought to a conclusion by arbitration, or mutual concession. Of course what is desired in every case is the truth; but if two chemists working in the same field, or on the same sample, do not agree, where is the truth? That there is a difficulty of this kind in the chemical analysis of iron and steel at the present time, we are confident few who are well informed on the state of affairs will be bold enough to deny. And it is not difficult to see why there should be discrepancy between chem-

<sup>1</sup> Read before the World's Congress of Chemists, August 21, 1893.

ists. The amounts of the various substances affecting the quality of these metals, is so small in many cases, the limits of the specifications upon which enormous quantities of iron and steel are bought and sold, are so narrow, that there is necessity for the very best analytical work. Furthermore, the time within which results, in order to be useful, must be obtained, is so short, and the quantity of work required of many laboratories is so great, that even if we assume that all chemists are equally able, there is still reasonable ground for expecting discrepancies. The demands made by the iron and steel industry upon analytical chemists, at the present time, are very great. But on the other hand, only those who are constantly using the results of chemical analyses of iron and steel, know how disheartening it is to be continually met with discordant results obtained by different chemists, and still worse how this discrepancy tends to throw doubt on the value of all applied chemistry. The manager of a large and successful iron works, who has himself during the past twenty years had no small share in helping on the development of the iron and steel industry in this country by applying chemistry to it, recently said: "What is needed to-day in the chemical analysis of iron and steel, is such an agreement between the different chemists working on the same sample that those who have to use the results of the analyses may have a reasonable ground for the belief that the work is near enough to the truth to be trusted." The time has certainly come when those who are engaged in the analysis of iron and steel must provide some means of eliminating this discrepancy and consequent doubt, or analytical chemistry must be content to take a position which I am sure none of us are willing to see it occupy.

This is no new state of affairs. The difficulty has been recognized before this, and steps have already been taken to overcome it. The formation of the "Committee on International Standards for the Analysis of Iron and Steel," which you are all familiar with, is a step in this direction. The plan of that committee it will be remembered, was to meet this difficulty of discrepancy in the work of different chemists, by furnishing each one, who desired it, a sample of a standard iron

or steel, in which the amount of the various constituents, was known, and thus furnish opportunity for him to check up his work. If any chemist felt in doubt about his work, or failed to get the same results as others, he could make an analysis of the standard sample, and if he obtained the known amounts of the various constituents he would be at liberty to conclude that his work was correct. If not, of course there is an error somewhere, which must be found and remedied.

At first thought, this plan seems to be entirely satisfactory, and it would almost appear as though nothing more was needed. If the work of that committee, it would seem, could be pushed forward to rapid completion, the difficulties due to discrepancy, which are now so annoying and vexatious, could be successfully managed, since it is obvious if we locate the difficulty, it must disappear.

Since this matter is so important, however, it may be wise not to reach a conclusion too soon. Is it really true that if we have in our hands a sample of steel in which the phosphorus, for example, is accurately known, and we make a determination of the phosphorus in this standard sample and get the known results, we are entitled to claim that our phosphorus work on other steels is accurate? Or again if we have a sample of steel or a series of samples, in which the carbon is known, and we check ourselves up by a comparison with these samples, are we entitled to claim that our other carbon work is correct? Or once more, if we are working on sulphur in iron and steel, and by our method and manipulation, we get exactly the same results on the standard steel or iron that it is known to contain, are we entitled to claim that our work on other samples is as close to truth as the standard sample.

At first sight it would seem as though these conclusions must follow. If we know how much phosphorus, carbon or sulphur a sample of metal contains, and with our appliances and methods and manipulation we get the known content of any of these constituents in the standard sample, it would almost seem that no other conclusion could follow, but that our work done with the same appliances, methods, and manipulation on other samples must be reliable and accurate.

We are inclined to think, however, that such a conclusion can hardly be successfully maintained. It is obvious, we think, that the condition in which the constituent, that we are working on, exists in the standard sample, has a most important bearing here. For example, if all the phosphorus in the standard sample, exists as phosphate, instead of phosphide, and some chemist who has been accustomed to determine phosphorus by dissolving his metal in hydrochloric acid, starts in to check himself up by comparison with the standard sample, it is clear that he may get exactly the same results as the standard is known to contain, and yet his work on other samples, in which the phosphorus exists, either wholly or in part in an unoxidized form, be worthless. Or again if the carbon in the standard sample is in such condition that the whole of it is shown by the color test, it is obvious that a chemist who checks himself up against the standard sample, would not therefore, necessarily, get correct results on other samples, unless they perchance all likewise had their carbon in the same condition in which it exists in the standard sample. Or still once more, if the sulphur in the standard sample exists in such form that it is all released as hydrogen sulphide by the method employed, and this is the characteristic feature of the method, it is obvious that however closely to the known content of the standard sample a chemist might get when working on this sample, his work by the same method on other samples, in which the sulphur is not all released as hydrogen sulphide, as is commonly the case in pig irons, would not be reliable and accurate.

These examples seem to us to indicate that standard samples in which the content of the various constituents is known never so accurately will not enable us to overcome the difficulty we are considering, independently of the method used. Obviously this is true, unless perchance the standard sample contains its various constituents in all the forms in which it is possible for them to exist. It, of course, may be urged that a series of standards, in which, taken as a whole, the various constituents exist in all possible forms would obviate the difficulty. But this means a multiplication of standards which might be very serious, and it means also the check by each chemist who is using the stand-

ards, of his method, manipulation, etc., against all of them, before he can be satisfied that his results are reliable. Perhaps we shall find that the difficulty can be obviated easier in some other way.

There is another phase of this case. Let us suppose that we have a standard sample in which the amount of carbon, phosphorus, sulphur, etc., is accurately known; that some chemist desires to check himself up; and that the method he uses is such that the difficulty discussed above in regard to the condition in which the various constituents exist in the metal is eliminated, does it now follow that, if the chemist in question gets the same results that the standard is known to contain, he is at liberty to conclude that his work on other samples is reliable? We are inclined to think that even under these circumstances the desired conclusion does not follow, for it may happen that the compensation of errors in the method and manipulation used, is such that on the standard sample, the correct result is obtained, while on a sample containing a different amount of the constituent which is being determined, this result would not follow. This point is too well recognized to need argument or illustration, and in the work of the Committee on International Standards an attempt has been made to meet this difficulty, by having a series of standards, differing from each other in the amounts of the various constituents. How large the number of standards would have to be, to completely overcome this difficulty, it is not easy to say, and for the purpose which we have in mind it is not necessary to go further into this phase of the discussion.

It must not be supposed that we are trying to belittle the work of the Committee on International Standards. One of us is a member of that Committee, and in our judgment, let it be said modestly, the work already done, and the results already obtained by that Committee, have more than justified its formation. But the point we have in mind is that although standard samples in which the amounts of the various constituents are known are valuable and perhaps essential, as an element in overcoming the discrepancy in chemical work, which is now so annoying, the possession and use of these standard samples alone, independently



of the method and possibly of other conditions, cannot be relied on to accomplish this desirable end.

A few words at this point upon the causes of discrepancy between the work of different chemists, may not be amiss. If we are right, the causes of discrepancy may all be comprehended under the following heads:

- (1) Lack of uniformity in the sample.
- (2) Impurities in the chemicals, or defects in the apparatus used.
- (3) The chemist.
- (4) The method.

The first of these causes of discrepancy is too obvious to need comment. If the samples worked on by the different chemists are not alike in the constituent in question, there is an obvious reason why the results should not be alike.

Also impurities in the chemicals or defects in the apparatus, are so clearly a sufficient cause for discrepancy between the work of different chemists, that no illustrations are needed.

Under the heading "the chemist," several points are involved. First, both the skill and the care with which the work is done are of prime importance in avoiding discrepancy. Not all men, and indeed not all who have studied analytical chemistry, seem to be fitted by nature to handle liquids and delicate apparatus with the skill essential to success. Possibly it is true that chemists, like poets, are born, not made. Second, many chemists although possessing manipulative skill in a high degree, do not seem to be willing to take the care and pains necessary to secure good work. If a method requires exact quantities of a reagent, or that a certain part of the work shall be done at a definite temperature, the chemist who pours in the reagent by guess or does not use a thermometer ought certainly not to be surprised if his results do not agree with those of another chemist, who puts upon his analysis, the additional labor required, in giving proper attention to these points. Third, it is clear that a part of the knowledge required in making any analysis, is furnished by the method. This is the function of the method, *i.e.*, to tell what is to be done, to describe the successive steps of the process, to state the amounts and kinds of reagents which must be used, and point out the precautions necessary to avoid error or

secure the desired end. But over and above this, every successful chemist must have a large amount of acquired knowledge, which the method does not give him. No single method can be a treatise on chemistry. Fourth, every working chemist knows the value of experience in enabling him to avoid error and secure good results. Everyone who is constantly making analyses knows that there are a very large number of little details, any one of which might injuriously affect the result, and which it is impossible to mention in connection with each method, which the chemist of experience looks after almost without thought, and which the chemist lacking in experience is very apt to overlook. Among these may be mentioned proving that the beakers or other apparatus are clean before starting, knowing that the distilled water is pure, seeing that the top of the reagent bottle is not contaminated with dust or other deposit before pouring out any of it, care that the reagents used have not deteriorated or changed from standing, and dozens of other little points, all small, but all essential. Fifth, there is another characteristic of the chemist which may have an exceedingly important influence on the results, *viz.*, a clear understanding or failure to do so, of the method step by step, and also the close application of the mind, or the reverse, to the analysis, while it is going on. The probability of a chemist getting reliable results with a method are very much diminished if he does not understand the changes which take place, when the various reagents are added, and the effect of each part of the manipulation on the final result. Without this knowledge there is great liability of something being done inadvertently which will vitiate the result. No description of a method can hope to be so minute as to obviate the necessity for this mental conception. Also, there is the greatest possible need of the close application of the mind to the work in hand, while it is going on. Many routine chemists seem to do their work with the mind in any other place than on their work. It is almost inevitable that error should creep in under these conditions. A trace of precipitate is lost, the washing is not quite clean, or perchance the analysis is contaminated by impurities from a contiguous beaker in which another operation is going on. Such chemists may

say truthfully, and usually do say, that they did everything exactly as the method required, and yet, as we can all see, their work is worthless.

That the method may be a cause of discrepancy between chemists few will be willing to deny. Some methods are inferior to others from indefiniteness of description, and some because the reactions involved are not quantitative to the same degree of accuracy, or perchance the insolubility of the final form is not as great in one method as in another. Whatever the cause, all methods are not equally accurate and without doubt some of the discrepancies of chemical work are due to difference of method.

How much of the present discrepancy in the analysis of iron and steel is due to each one of these causes, it is perhaps difficult to say. Some are inclined to think the lack of uniformity in samples is a very fertile source of differences in results, and there is much information pointing in this direction. Others are inclined to think that the various causes of discrepancy, which we have treated above, under the heading, "the chemist," are the principal source of the difficulty. Poorly trained, overworked and inferior chemists, they say cannot well do anything but inferior work, and when the results of such chemists, are brought face to face with a much higher grade of work done by a much better class of chemists, it is no wonder that there are discrepancies. Still others blame the chemicals and the method. Which is the most potent cause, however, is not the real question. What we want to know is, first, what can be done to reduce the discrepancies to a minimum, and after this has been accomplished, to provide some means by which the discrepancies can be reconciled, and the error of one or both of the results be eliminated. It is manifestly absurd to expect that the time will ever come when there will be no discrepancies between the results obtained by different chemists. To do this would require uniform samples, absolutely pure chemicals, chemists incapable of error, and methods which give absolutely accurate results. The most that we can hope to accomplish is to provide some means by which, when discrepancies do occur, it can be decided which, if either, of the two results is the more

correct, and consequently the more entitled to be trusted and used.

Let us now look at the causes of discrepancy, mentioned above, and see whether there is any way out of the difficulty when the discrepancies are due to any of these causes.

If two chemists do not get the same results, due to the fact that the samples worked on do not actually contain the same amounts of the various constituents sought, there is a very simple way of managing the difficulty, *viz.*, exchange of samples. This is common practice to-day, and is usually the first thing done, when disagreement of results is announced. If we may trust our experience, this is all that is necessary to be done in very many cases. Also, if the discrepancy is due to impurities in the chemicals, or to defects in the apparatus, it is usually not difficult to locate the trouble. An examination and test of the chemicals, an exchange of the chemicals, or the change of, or the setting up of a new piece of apparatus, by one or both will usually show which is in fault. This likewise has been done in a number of cases, with more or less valuable results. For the discrepancies which are due to the various causes mentioned above under the heading, "the chemist," there is likewise a remedy not difficult to apply, *viz.*, to have the two chemists make an analysis in presence of each other. This is not uncommon practice in assaying. That lack of skill and care, lack of knowledge and experience, lack of attention, etc., would be eliminated when two chemists who disagree are required to work in the presence of each other, is too obvious to need further comment.

There is another way of handling the discrepancies due to two at least of the causes mentioned above, that is those arising from impure chemicals and defective apparatus, and those grouped under the heading, "the chemist," *viz.*, the plan proposed by the Committee on International Standards. If the discrepancy is due to an actual difference in the sample, we see no way of locating the difficulty, except to exchange samples. But if discrepancy arises between chemists from impure chemicals or bad apparatus, or from the chemist, himself, it would seem that an analysis by each of a standard sample in which the

amount of the substance sought was known, would show whether the work of either or both of the two disagreeing chemists was faulty from either of these causes.

So far therefore, as discrepancies are due to three of the four causes given, there seems to be no serious difficulty in managing them. A sincere disposition on the part of the disagreeing chemists to get at the truth, will soon find the trouble. If it is due to method, however, the difficulty is not so easily overcome. Two chemists of equal ability perhaps, and certainly both equally honest, obtain results on the same sample which do not agree, and the disagreement is due to difference of method, who is going to say which is right, and which results should be used? Both have used good methods, which have been approved, and both are equally confident in, and tenacious of their own results, and both have an equal right to their opinion and belief.

This state of affairs seems to us to be a genuine difficulty, which at present there is no means of overcoming. We have tried to show that the proposed international standards for the analysis of iron and steel, although undoubtedly a step in the right direction, and a most valuable aid, still do not quite meet the difficulty. We therefore have the honor to suggest as a remedy, the establishment of standard methods for the analysis of iron and steel. If methods can be found, which in the hands of different chemists, will give the same results, and which are sufficiently rapid and accurate to be available and useful, and then an agreement be obtained to regard these methods as standard, and to use them as such until they are modified by the same authority that established them, we are confident that a long stride will be taken in the direction of overcoming the difficulties which are now so vexatious and annoying, in the analysis of iron and steel. Can such methods be found, and can this agreement be obtained? We are of the opinion that for most, if not all, of the constituents usually determined in iron and steel, satisfactory methods are now available. It is for this body to say whether they will do anything to help forward the needed agreement.

Before attempting to present for your consideration any proposed standard methods, it may not be amiss to discuss two or

three points a little further. First, let us suppose that there is no known method that will satisfactorily fill all the requirements of a standard method. It is satisfactory in most respects, but not in all. What shall be done in such a case. We are inclined to think that this will not introduce any insurmountable difficulty. If the only known method, for example, that is sufficiently rapid to be available as a standard, is not quite as accurate as another, which is too slow for use as a standard, it will of course be requisite for all to agree to accept the results as given by the less accurate method, until a better can be obtained. We are very strongly of the opinion that as far as the applications of chemistry to commercial transactions are concerned, this will not be a serious matter. If there were standard methods for the analysis of iron and steel, so recognized by the profession, it would not be long before all contracts involving the chemistry of iron and steel, would contain a clause specifying that the analyses should be made in accordance with the standard methods. Of course, those making the contracts would know of the inaccuracy in the standard method, and would be able to allow for it, and we are confident that the value of agreement, and the avoidance of dispute owing to discrepancies, would be much preferred in the commercial world, to such a straining after accuracy as makes a method unusable.

Second, it may be urged that the establishment of standard methods would interfere with the progress of chemistry. The method being fixed, and the results being accepted without question, there would be no stimulus to obtain better results, and consequently no progress. In opposition to this view we would say that while progress may be stimulated in a measure by the antagonism of two chemists who do not agree, we are inclined to think that practically such antagonism often results in a squabble, rather than real progress and also that most of the progress in chemistry thus far has arisen in another way. Usually those who develop and publish new methods or modifications of old ones, do so, not so much to vanquish an antagonist, as to help themselves forward in their own work, or to obtain from their fellows, by publicity, the recognition which they feel is due. Both these stimulants to progress

are fully as strong with standard methods in existence as without. Indeed, it may fairly be queried whether there would not be a stronger stimulus to upset or modify a standard method than would be the case if there were none. Certainly the reputation which would come to one who successfully changes or replaces a standard method, would be greater than that which would fall to one who simply offers a new method or modification, which must stand on its own merits among a lot of others independent of any organized action.

Third, what is the sphere of a standard method? Can a standard method be used for all purposes, or do the qualifications which make it available for one class of work render it unfit for use in another? This evidently is a matter of some importance. If the requirements of one kind of work are such that no method can be found that will fill these requirements and at the same time meet the requirements of another class of work, it is obvious that one class of work or the other will have to get along without the proposed standard methods. Let us examine into this a little. The chemical work done on iron and steel, may perhaps be fairly divided into three classes. (1) Quite a large amount of chemical work is done in connection with steel works, for the guidance of the manager or superintendent in making the product. The special requirement of this kind of work is speed, since it is impossible to hold the metal in the furnace for any long period of time. (2) By far the largest portion of the chemical work done on iron and steel at the present time is that in which commercial transactions are more or less directly involved, including under this head all analyses connected with the applicability of raw materials to make a certain kind of product, and all analyses having any relation to the sale of the output, and its acceptance or rejection by the consumer. The special requirement of these analyses is speed and accuracy. (3) A considerable amount of chemical work is done each year which may fairly be classed as investigation or research, such as studies made for the purpose of increasing the output of any plant, or an inquiry by those interested in the possibility of making any desired product, or an investigation by a consumer as to what kind of metal will give best

results in any given surface. The special requirement of this work is accuracy. If now no method can be found which will give the accuracy required in an investigation, along with the speed essential in the operation of a steel works, it is obvious that the same standard method cannot be used in both cases. Fortunately some of the best and most accurate methods known are likewise sufficiently rapid, so that in most cases the standard will probably be applicable to all classes of work ; but unfortunately at the present time, this is not true of all. It will undoubtedly be the delightful work of those chemists who have time and opportunity, to develop in the near future methods for all the various constituents of iron and steel, which will be applicable to all purposes; but at the present moment we are compelled to ask for what class of work shall we attempt to prepare standard methods ?

Undoubtedly there is a reasonable opportunity here for a difference of opinion. Perchance some will think the method required for an investigation is none too good to be adopted as a standard. Others may think, perhaps, the methods in common use in steel works are sufficiently good. Our own idea is that the criterion by which a method should be judged, as to its fitness as a standard at the present time, is its applicability for use in commercial transactions. If it is sufficiently rapid for such use, for as all know, in commercial transactions time is money, and sufficiently accurate so that both parties to a transaction are willing to abide by its decisions, when their pockets are involved, it is a sufficiently good method to be regarded as a standard, at least until something better can be proposed. This criterion may seem to some to be ignoble, and to derogate from the dignity of chemistry as an exact science, but it must be remembered that in the chemical analysis of iron and steel, questions of pure science are involved in only a very limited degree. We are using chemistry as a means to an end, and however delightful it may be to pursue the truth, for the truth's own sake, this is not the problem which we have before us. Furthermore, we are confident that those who think the class of chemical work done on iron and steel where commercial transactions are involved is inferior and of low grade, will if they make a little careful investigation, find that this kind of work is very much



better than they had supposed. The reasons why this should be so are not hard to find. (1) The practice which chemists who are engaged in commercial work get is very great, and every working chemist knows how much more reliable and uniform his results are after he has had considerable experience and practice with a method, than when it is new to him. (2) By far the largest portion of the analyses made where commercial transactions are involved are made with the thought in mind that the results will be questioned by another chemist on the opposite side of the transaction. In fact, a very large number of the results obtained by the chemist of the buyer, are met with results obtained by the chemist of the seller, and if the results do not agree, a third entirely impartial chemist is often called in to decide between the two. The value of this criticism of results on the accuracy of chemical work must be evident to all.

Fourth, what are the requirements of a standard method?

First, obviously it must be sufficiently accurate. But what is sufficiently accurate? Accuracy is a question of limits. No method gives results which are absolutely accurate. Even many of the atomic weights, upon which the very best possible chemical work has been done, are still in dispute. Furthermore, it hardly answers the question to say that sufficiently accurate is the highest accuracy that any known method will give, since other qualifications, some of which unfortunately are antagonistic to the highest possible accuracy, are likewise requirements of a standard method. It is evident that the line must be drawn somewhere, and more as a means of developing the opinion of the profession on the matter, than as desiring to dictate to them, we would suggest that a method which in the hands of different good chemists of experience will give three or four results on the same sample, agreeing within the following limits for the six constituents usually determined in iron and steel, is sufficiently accurate to be regarded as a standard method, *viz.*:

	Per cent.
Carbon, within .....	0.01
Phosphorus, within .....	0.005
Sulphur, within .....	0.005
Silicon, within .....	0.01
Manganese, within .....	0.01
Copper, within .....	0.005

We are confident that commercial transactions will readily adapt themselves to these limits and that if the discrepancies between different chemists do not exceed these limits no questions will ever be raised.

Second, a standard method must be sufficiently rapid. But here likewise the same question arises, What is sufficiently rapid? And here again it can fairly be said, this is a question of limits. Of course the desire, both on the part of the chemist and on the part of those who are to use the results of the analysis, is to have the chemical work done in the shortest possible time. For the chemist rapid methods save both time and effort; and in commercial transactions it is often of the greatest possible moment to have the results of analysis quickly. Furthermore, it is not enough to say that if business men want to use the results of chemical analysis in their business, they must simply allow time enough to have the analysis made. Undoubtedly this is true as an abstract statement, but it is also true that if three or four days or a week must elapse before the results of analysis are available, thousands of analyses will never be made. The analytical chemistry of to-day must adapt itself to the requirements of to-day, or it will have no work to do. And this brings us again to the question, What is a sufficiently rapid method? We are inclined to think that methods are now available for most, if not all the substances usually determined in iron and steel, which will enable results to be obtained the same day, if the sample is taken in hand in the morning. With some of the methods half a day suffices. We are also strongly of the opinion that these limits will be fairly satisfactory to those who are most required to use the results of analyses. In order to have something definite, and not beat the air in our discussion, we would suggest that no method be regarded as standard which will not give a result in one working day.

Closely connected with this point, is a third requirement of a standard method, *viz.*, it should be simple, or in other words, not be so laborious that one chemist can only turn out a very small amount of work in a day. Even though a result can be obtained in one day by a method, if it requires such close application and so much work on the part of the chemist that when

night comes he has only the one analysis, obviously the cost of that analysis will be much higher than if a dozen or twenty results could be obtained in the same time. This is evidently a matter which must receive consideration. If the cost of an analysis is high, much fewer analyses of that kind will be made, than if the cost is more reasonable. It is perhaps not too much to say that this point has in the past seriously retarded the growth of analytical chemistry. But it is obviously difficult to say, where to draw the line in this matter of the output or capacity of one chemist, as affected by his method, since the magnitude of the transaction in which the results of the analysis are used clearly has an influence. It is perhaps sufficient to direct attention to it as having an important bearing on the possibilities of a method being regarded as standard.

A fourth requirement of a standard method is, it must be so well understood, and the control of the conditions affecting the result must be such that the results are uniform, that is, that three or four or half a dozen analyses made on the same sample by the same chemist, must agree so far as agreement is affected by the method. It is common experience that some methods are not as reliable in this respect as others. Sometimes good results are obtained with a method, and sometimes anomalous ones appear. This may be due to the fact that the method is not well worked out, that is, all the conditions affecting the result have not been sufficiently studied. It may be due again to the fact, that the control of the conditions is difficult to obtain. The reaction in a subsequent part of the operation, may be affected by some reagent, previously used, and which it is either difficult to remove completely, or to be sure that it is all removed. Furthermore, some methods have a still more radical defect, *viz.*, the reactions on which they are founded are apparently quantitative for certain conditions, in which the substance sought exists in the material being analyzed, but this is not true for all the conditions of the material. We will not take your time to cite examples of these various peculiarities of methods. It is obvious, however, that a standard method should not be defective in any of these respects.

Closely connected with this is a fifth and final requirement of

a standard method, *vis.*, different chemists must be able to get concordant results, so far as the results are a function of the method. If the standard method is a reliable one, as has just been explained, the ability of different chemists to get concordant results with it, so far as these results depend on method, is evidently a question of description. Many methods suffer from indefiniteness of description. Too much is left to the judgment and experience of the chemist, and it seems reasonable to suppose that some of the differences between good chemists using the same method may be explained in this way. Obviously the description of a method is affected sometimes by the peculiarities which are to be described. We all know that some characteristics of a method are exceedingly difficult of description. For example, suppose a precipitate is perceptibly soluble in the wash water. It is clear that over washing is as much to be avoided as under washing. But how to define just the point at which the washing should stop, in many cases, is not easy. Again many methods are insufficiently described. The amounts of the different reagents to be used are not definitely stated, and precautions necessary to be taken are not clearly pointed out. Since, as has already been stated, no method can be a complete treatise on chemistry, it is reasonable to suppose that those who are describing any method are naturally in doubt how much to give and how much to withhold. It is clearly not easy to draw the line, and if standard methods for the analysis of iron and steel are ever adopted, it is probable that this will be one of the difficult points to cover.

But this paper is, we fear, occupying far too much time and space; and yet a few words, showing what has already been done in developing the proposed standard methods, are perhaps essential.

About a year ago in connection with our regular work for the corporation with which we are employed, it became necessary to prepare specifications for steel for various uses in which the limits on some of the constituents usually determined in this metal were pretty close, and, judging from our past experience, we foresaw that when we came to receive the material on these specifications, and to examine each shipment as is our custom,

there would be difficulty due to discrepancy between ourselves and the chemists at the various works where the material was made. The various causes of discrepancy were gone over and the same conclusion reached that is expressed above, *viz.*, that the discrepancies arising from all causes except the method, could be successfully managed. How to meet this difficulty however, was a problem. The work of the Committee on International Standards was not yet complete, and no standard methods had yet been agreed upon. After considerable thought we decided to put the methods by which the various constituents should be determined in print, in minute detail, and then make these printed methods a part of the contract on which the material was bought. In pursuance of this plan, three methods have already been printed, *viz.*, "Phosphorus in Steel," "Carbon in Iron and Steel," and "Sulphur in Steel." It will be observed that the ground is as yet only partially covered. It should also be stated that very little experience has been had with any of the methods as yet. If this congress had come a year later, it would have been possible to say something about a part, at least, of the methods from actual experience with them in practical work. We are not rash enough to expect or even hope that the methods which we have tried to put into definite shape to enable us to meet an emergency which has arisen in our own work, will be accepted by the profession as standard methods for this important branch of analytical chemistry. Nor do we claim any special originality in connection with the methods. We have freely appropriated any work we could find anywhere that was applicable, have made a good many analyses to check up individual points, and have in a limited way, tested the methods in the form in which they are presented. It is our intention to cover in the way described above that part of the analysis of iron and steel which comes within the scope of our work. Such as they are, these methods are offered as a starting point from which to develop standard methods, with the sincere hope that this body will take some action, looking toward the accomplishment of this greatly to be desired end.

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**METHOD OF DETERMINING PHOSPHORUS IN STEEL.<sup>1</sup>****OPERATION.**

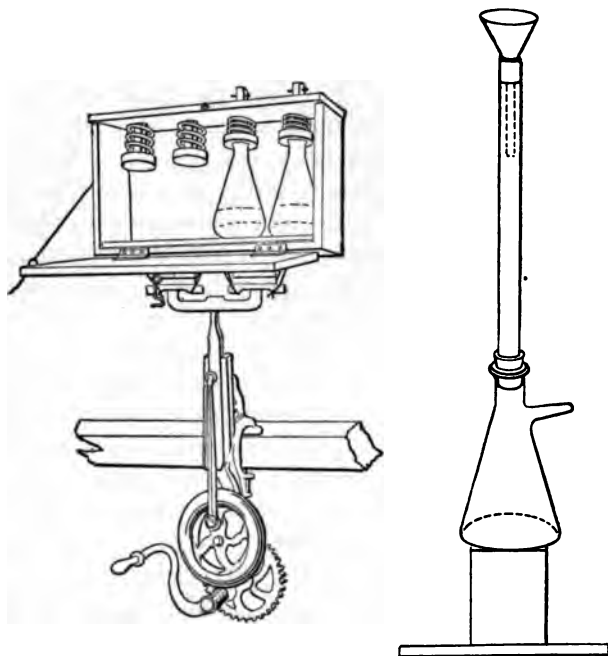
Put one gram of the steel in a ten to twelve ounce Erlenmeyer flask and add seventy-five cc. of nitric acid (1.13 sp. gr.). When solution is complete, boil one minute and then add ten cc. of oxidizing potassium permanganate solution. Boil until the pink color disappears and binocide of manganese separates, remove from the heat and then add crystals of ferrous sulphate, free from phosphorus, with agitation until the solution clears up, adding as little excess as possible. Heat the clear solution to 185° F. and add seventy-five cc. of molybdate solution, which is at a temperature of 80° F., close the flask with a rubber stopper and shake five minutes, keeping so enclosed during the operation that it will lose heat very slowly. Allow to stand five minutes for the precipitate to settle, and then filter through a nine cm. filter and wash with acid ammonium sulphate solution, until ammonium sulphide tested with the washings, shows no change of color. Dissolve the yellow phospho-molybdate on the filter in five cc. of ammonia (0.90 sp. gr.) mixed with twenty-five cc. of water, allowing the solution to run back into the same flask and thus dissolve any yellow precipitate adhering to it. Wash until the washings and filtrate amount to 150 cc., then add ten cc. strong C. P. sulphuric acid and dilute to 200 cc. Now pass the liquid through a Jones reductor or its equivalent, wash and dilute to 400 cc. and then titrate in the reductor flask with potassium permanganate solution.

**APPARATUS AND REAGENTS.**

The apparatus required by this method needs no especial comment except perhaps the shaking apparatus and the modification of the Jones reductor. Accompanying cuts illustrate these two. The shaking apparatus, as will be observed, is a modification of an ordinary milk shake machine, and is arranged to shake four flasks at a time, which is about all one operator can manipulate without the solutions becoming too cold. The cut is about one-twelfth the actual size of the apparatus. The

<sup>1</sup> [This method forms part of the specifications for steel of the Pennsylvania Railroad Company. It has been published in the *Journal of Analytical and Applied Chemistry* for February, 1893, p. 108, but on account of its importance is here reprinted in full.—Ed.]

flasks containing the solutions rest on a sheet of India rubber about one-fourth inch thick and are held in position by the coiled springs as shown. There is a recess in the spring arrangement to receive the cork of the flask. In the absence of a shaking apparatus, the flasks may be wrapped in a towel and shaken by hand. Of course during use the door of the box is closed, the cut showing it open so that the interior may be seen. The modified reductor seems to work equally as well as the more elaborate apparatus. The cut is about one-eighth actual



size. As will be seen the tube is fitted with two rubber corks, the top one of which holds the funnel and the bottom one a small tube which also fits into the rubber cork in the flask. Next to the bottom cork in the tube is a disc of perforated platinum; then about three-fourths of an inch of clean white sand; then another perforated platinum disc, and then the tube is nearly filled with powdered zinc. At least half the zinc may be used out before it is necessary to re-fill.

Burettes can usually be obtained in the market which are sufficiently well made and graduated with sufficient care, so that their error can be ignored. Of course this point should not be overlooked.

The specific gravities of the reagents given are essential and the temperature at which the figures are correct is 59° F. In determining these gravities it is best to use a Westphal balance, but failing this a sufficiently delicate hydrometer can be used.

The oxidizing permanganate of potash solution is made as follows: To two liters of water, add twenty-five grams of C. P. crystallized permanganate of potash, and allow to settle before using. Keep in the dark.

The molybdate solution is made as follows: Dissolve 100 grams of molybdic acid in 400 cc. of ammonia (sp. gr. 0.96) and filter. Add the filtrate to 1000 cc. of nitric acid (sp. gr. 1.20). Allow to stand at least twenty-four hours before using.

The acid ammonium sulphate solution is made as follows: To one-half liter of water add 27½ cc. of ammonia (0.96 sp. gr.) and then add twenty-four cc. strong C. P. sulphuric acid, and make up to one liter.

The permanganate of potash solution for titration is made as follows: To one liter of water add two grams of crystallized permanganate of potash, and allow to stand in the dark not less than a week before using. Determine the value of this solution in terms of metallic iron. For this purpose 150 to 200 mgms. of iron wire or mild steel are dissolved in dilute sulphuric acid (ten cc. of strong C. P. acid to forty cc. of water) in a long necked flask. After solution is complete, boil five to ten minutes, then dilute to 150 cc., pass the liquid through the reductor, and wash, making the volume up to 200 cc. Now titrate with the permanganate solution. It is of course essential that the amount of iron in the wire or soft steel should be known. The standard in use in the Pennsylvania Railroad laboratory is a mild steel in which the iron is known by determining carbon, phosphorus, silicon, sulphur, manganese, and copper, and deducting the sum of these from 100 per cent. Not less than two independent determinations should be made and three are better. The figures showing the value of the permanganate solu-



tion in terms of metallic iron should agree to one-hundredth of a milligram in the different determinations. A very satisfactory method of making and keeping permanganate of potash solution is as follows: Have a large glass bottle holding say eight liters and two of half the size. Paint the outside of these bottles with several coats of black paint or varnish. Fill the large bottle with the standard solution, and after it has stood a proper time, fill one of the smaller bottles from it without shaking, and standardize. At the same time fill the second small bottle, and refill the large one. When the first small bottle is exhausted standardize the second one and fill the first from the stock. When this is exhausted standardize the first again and fill the second from stock, refilling the stock bottle again and so on. By this means a constant supply of sufficiently matured permanganate is always available. Of course if the consumption is very large, larger bottles or more of them may be required. Since changes of temperature affect the volume of all solutions, it is desirable that the permanganate solution should be used at the same temperature at which it was standardized. With the strength of solutions above recommended, if the permanganate is used at a temperature of 20° F. different from that at which it was standardized, the error amounts to less than 0.001 per cent. on a steel containing 0.10 per cent. of phosphorus.

#### CALCULATIONS.

An example of all the calculations is given herewith. The soft steel employed in standardizing permanganate of potash solution in the Pennsylvania Railroad laboratory contains 99.27 per cent. metallic iron. 0.1498 gram of this contains therefore  $(0.1498 \times 0.9927)$  0.1487064 gram of metallic iron. This requires 42.9 cc. permanganate solution or one cc. of permanganate solution is equal to  $(0.1487064 \div 42.9)$  0.003466 metallic iron. But the same amount of permanganate solution used up in producing the characteristic reaction in this amount of metallic iron, will be used up in reaction with 90.76 per cent. of the same amount of molybdic acid. Hence one cc. of permanganate solution is equivalent to  $(0.003466 \times 0.9076)$  0.003145 gram of molybdic acid. But in the yellow precipitate obtained as above described, the phosphorus is 1.90 per cent. of the

molybdic acid. Hence one cc. of permanganate solution is equivalent to  $(0.003145 \times 0.0190) 0.0000597$  gram of phosphorus. If, therefore, in any sample of steel tested as above, the yellow precipitate requires 8.6 cc. of permanganate, the amount of phosphorus in that steel is  $(0.0000597 \times 8.6) 0.051$  per cent.

#### NOTES AND PRECAUTIONS.

It will be observed that the method given above oxidizes the phosphorus in the iron by means of nitric acid, completes and perfects this oxidation and possibly neutralizes the effect of the carbon present by means of permanganate of potash, and then separates the phosphoric acid from the iron by means of molybdic acid. The molybdic acid in the yellow phospho-molybdate is subsequently determined by means of permanganate of potash, the phosphorus being determined from its relation to the molybdic acid in this precipitate. The method given above applies to steel and wrought iron, but is not yet recommended for pig iron.

It is hardly necessary to say that all the chemicals and materials used in the analysis are assumed to be free from impurities that will injuriously affect the result.

1.13 sp. gr. nitric acid apparently oxidizes the phosphorus just as successfully as a stronger one, while by its use solution is sufficiently rapid, and there is less trouble during the subsequent filtration due to silica.

If the solution is boiled one minute after solution is complete it will use up much less permanganate than if the preliminary boiling is omitted.

Care should be taken to secure a crystallized ferrous sulphate free from phosphorus. The commercial salt is apt to be contaminated. It should be added in small crumbs so as to avoid excess. If too much has been used, a few drops of permanganate can be added to oxidize it.

The temperature at which the molybdate solution is added to the iron solution and the resulting temperature, have an influence on the result. The directions should be closely followed, a good thermometer being used to determine temperatures. Never add the molybdate solution and then heat.

In washing the yellow precipitate it shows some disposition

to crawl up to the top of the filter. Care should be taken therefore to have the filter fit the funnel so closely that even if the precipitate does crawl over the top it will not be lost while washing the filter completely to the top. It is very easy to leave enough molybdic acid in the top of the filter, even though the washings are tested, to cause an error of 0.005 per cent. in the determination.

The amount of molybdate solution given above is enough to convert all the iron into molybdate, and still leave enough to carry down the phosphorus.


It is best to make up molybdate solution frequently as it slowly changes on standing. We think it inadvisable to use a molybdate solution over ten days old. It is best to keep the molybdate solution in the dark at a temperature not above 80° to 85° F. The solution should always be filtered before using. Much of the so-called molybdic acid of the market is molybdate of ammonium or molybdate of some other alkali. This fact cannot be ignored in making up the molybdate solution. A series of experiments with various molybdic acids and alkaline molybdates obtained in the market indicates that if the amount of molybdic acid in the solution is that called for by the formula, irrespective of whether this amount is furnished by pure molybdic acid or any of the commercial molybdates referred to, the result will be much nearer the truth, than if this is not done. Good molybdic acid is best, but the alkaline molybdates can be used. The amount of molybdic acid in these molybdates can readily be determined by dissolving 0.1000 gram in 100 cc. of water to which a little ammonia has been added, and filtering. Now add ten cc. strong C. P. sulphuric acid, dilute to 200 cc. and pass through the reductor. Wash and dilute to 400 cc. and titrate with permanganate. The method given in the calculation above enables the amount of molybdic acid to be determined.

It is not advisable to make up the acid sulphate of ammonium solution for washing the yellow precipitate by using sulphate of ammonium and sulphuric acid, as the commercial sulphate of ammonium frequently contains phosphorus in some form.

The description and measurements given along with the cut of the modified reductor above will perhaps enable any one to

make a suitable apparatus for themselves if they desire. The powdered zinc used is that which will pass through a twenty mesh sieve, and not pass through a thirty mesh sieve. It may be obtained from Baker & Adamson, Easton, Pa. It is essential before using the reductor to pass two or three blanks through, containing all the materials except the substance being analyzed, and then titrate these blanks. The last two blanks should agree exactly, and the amount of permanganate used up by the last blank should be deducted from the final figure obtained on titration of the substance being analyzed. This preliminary preparation of the reductor is essential after a new charging with powdered zinc, and also equally essential after the reductor has stood idle even over night. The rate at which the material passes through the reductor can be controlled somewhat by the suction. The apparatus is very efficient, and there seems little danger of too rapid a rate, but it is of course essential that the reduction should be complete. The properly reduced yellow precipitate solution should be green or slightly so, depending on the amount of molybdic acid present. A trace of "port wine" color in the reduced solution before titration with the permanganate indicates lack of complete reduction and renders the result of the analysis doubtful. In case of incomplete reduction pass the liquid through the reductor again. If the rate is somewhat slow and the solution being reduced somewhat warm, hydrogen gas enough may be generated to throw some of the liquid up against the sides of the tube above the zinc, and also bubble up through the liquid in the funnel. Care should be taken that this latter does not result in loss, and that the liquid adhering to the sides of the tube is removed by the subsequent washing.

There is some analytical evidence when using the method described above, that a portion at least of the arsenic which may be present in a sample of steel under examination, is precipitated along with the phosphorus, and counts as such in the final result. Until some simpler method of overcoming this difficulty than any at present known has been devised, and until the injurious effect of arsenic on steel has been demonstrated to be so small that arsenic can safely be ignored, the results obtained



by the above method, will be regarded as the phosphorus content of the various steels purchased in accordance with Pennsylvania Railroad specifications.

Samples of steel in which the phosphorus has been determined will be sent to parties asking for the same in order to enable them to make such comparisons as they may desire.

In formulating the method given above, the published work of Emerton, Wood, Drown, Hundeshagen, Colby, Shimer, Handy, and Jones, has been freely consulted and used. It would be difficult to state in detail what is due to each.

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#### METHOD OF DETERMINING CARBON IN IRON AND STEEL.

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##### OPERATION.

Put three grams of fine borings of the iron or steel in a sixteen ounce beaker or pint dissolving jar, and add 200 cc. of an acid solution of the double chloride of copper and potassium which is at a temperature not above 100° F. Allow to dissolve, taking pains to agitate the liquid during solution. As soon as the separated copper has all disappeared, allow to stand a little while to settle if necessary, and then pour the supernatant liquid, on an asbestos filter in a platinum boat, taking pains at the last to pour out all the liquid, and at the same time leave as much of the separated carbon in the beaker or dissolving jar as possible. Now add about ten cc. of dilute hydrochloric acid (sp. gr. 1.1) to the beaker or jar and so manipulate that this acid shall touch all parts of the beaker or jar which has been in contact with the solvent liquid. Pour this acid on the filter, and wash the carbon out of the beaker or jar by means of a wash bottle containing acid of the same strength. Continue the washing with the acid until all color has disappeared from the washings, and then wash with water until the washings no longer react for hydrochloric acid. After the washing is complete the filtrate should be poured into a large beaker and diluted with clean water, and acid added if necessary to hold the sub-chloride of copper in solution, until it is possible to see whether any carbon has escaped the filter. If any is found, of course the liquid must be passed through the filter again, or

the material all thrown away, and a fresh start made. Dry the carbon at a temperature not above 212° F., and then place the boat with the dried material in it in the combustion furnace. While the drying is going on, weigh the absorption potash bulb and prolong, which have been previously prepared as described below, and place them in their proper position, in connection with the combustion train, which has likewise been previously prepared as described, and in which the preheating furnace has been lighted long enough, so that its porcelain tube is fairly red for at least five or six inches of its length. Start the combustion by turning on enough burners at the front end of the combustion tube to embrace about three inches of it with flame, and at the same time see that the connection to the air gas holder is closed, and then open the connection between the oxygen gas holder and the combustion tube, and then adjust at the aspirator so as to allow about three bubbles a second to show in the absorption potash bulb. As soon as the combustion tube above the burners already lighted becomes perceptibly red, turn on enough more burners to embrace a couple of inches more of the tube and allow this portion likewise to become perceptibly red. From this point turn on one or two burners at a time, allowing the tube above them to get red before turning on more, until enough have been turned on to heat the tube red a couple of inches toward the rear end from where the boat lays inside. Continue the combustion after the last burner is lighted about fifteen minutes for steel and not less than thirty minutes for pig or cast iron, taking care to keep the flow of oxygen to the combustion tube sufficient to maintain a slight pressure in this tube, and at the same time not allow over about three bubbles per second to pass the absorption potash bulb. After the burning is completed, turn down the gas supply to the burners by means of a cock one-half, or turn out every other burner so as to allow the combustion tube to cool down slowly, and then shut off the oxygen supply and turn on the air supply for aspiration. Allow not less than a liter of air to pass through the absorption potash bulb, at a rate of not over three bubbles a second. While the aspiration is going on diminish the gas supply to the burners by means of the cock, or turn out ad-

ditional ones as fast as the tube will stand it. When the aspiration is complete, detach the potash bulb and prolong from the furnace, close the ends with rubber caps, and place in the balance case. Allow to stand fifteen minutes, and then weigh.

#### APPARATUS AND REAGENTS.

We prefer to use in dissolving the iron or steel a jar of thick heavy glass, rather than a beaker. The jars we have found useful hold about a pint and have a nose for pouring. One is shown in Figure 1.

The agitating apparatus shown in Figure 2 consists, as will be seen, of a slight modification of the well-known stirring machine shown in "The Chemical Analysis of Iron," by A. A. Blair, arranged to stir twelve beakers at once. The shaft carrying the stirring rod consists of a five-eighth inch diameter brass tube, carrying at the bottom a disk which revolves with it. This disk, which is four and one-half inches in diameter and slightly turned up at the edges, serves very satisfactorily as a cover to the beakers in place of the perforated glass plate. The disk should revolve within about one-eighth inch of the top of the beakers. The hole in the brass tube used as a shaft serves to receive the cork carrying the glass rod which, as is observed, is bent at the lower end so that it will just nicely revolve in the beakers or dissolving jars. The frame of the apparatus is made of wood about eleven and one-half inches wide and about forty inches long. The two horizontal parts at the top of the frame are perforated with five-eighth inch holes five inches apart each way, which holes, without any bushing, serve as bearings for the hollow tubular shafts. The top of each shaft carries a wooden pulley four inches in diameter, which has a brass bushing and set screws by means of which it is fastened to the shaft. Brass washers between the pulleys and the top of the frame carry the weight of the revolving parts and diminish the friction. A little tallow and graphite on the rubbing surfaces is also valuable for the same purpose. We use an electric motor for power, and the glass stirring rods revolve about four hundred revolutions per minute. By taking care to wash the stirring rods both before and after using they may be adjusted once for all and left in position. The beakers or dissolving jars are supported on

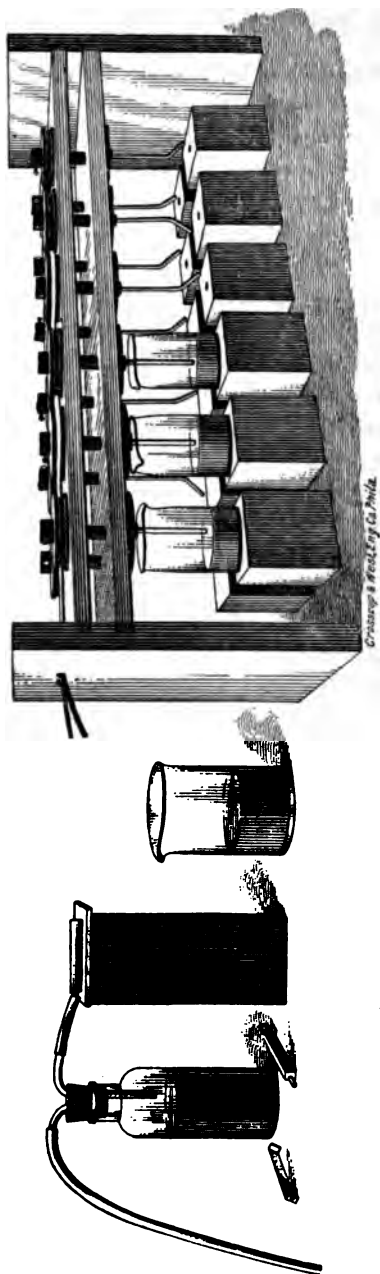


FIGURE 1.

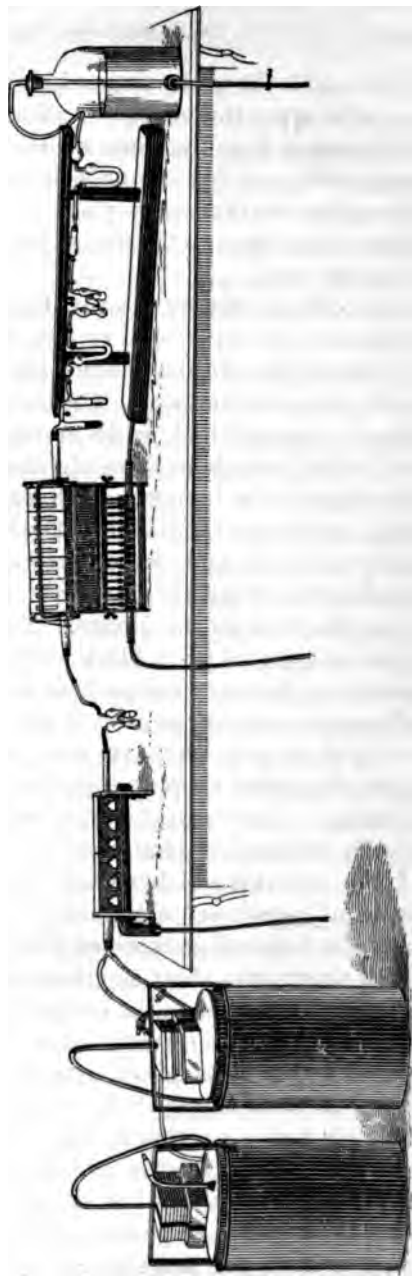
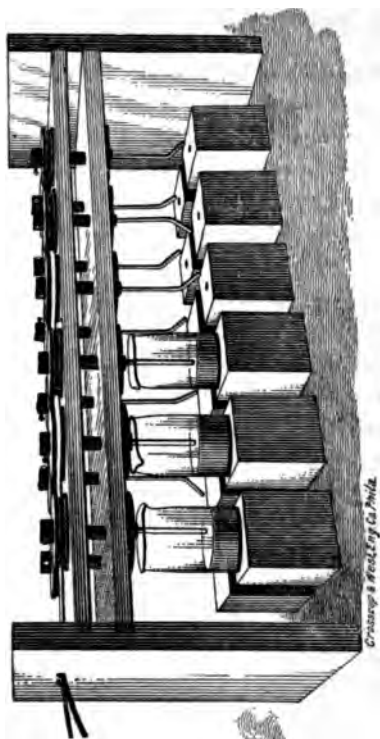


FIGURE 3.

FIGURE 2.





wooden blocks of the proper height, which blocks are movable, so as to allow the beakers or dissolving jars to be put in position, or removed from the same without difficulty. With this stirring apparatus and the amounts of material previously prescribed, complete solution takes place in from seven to forty-five minutes, depending on the size of the borings and the nature of the steel or iron.

As will be seen by the cut, Figure 1, the devices for filtration consist of a receptacle to receive the filtrate, which is connected at the outlet with the exhaust pump or suction, and at the inlet with the platinum boat. The platinum boat is about three inches long, one-half inch wide at top, seven-sixteenths inch wide at bottom and about three-eighths inch high. It is fitted with a perforated false bottom, which leaves a clear space underneath it of about one-eighth inch. The boat is also fitted with a tubular opening at one end, which serves both as a means of connection to the inlet of the filtrate receptacle, and also as a passage-way from the boat for the filtrate. The boat rests on a clean glass plate, supported on a block, which glass plate serves to catch anything that may escape from the boat during filtrations with a chance to recover the same if desired. This form of boat is as efficient as any we have ever seen, and seems to give less difficulty about keeping tight joints than those with perforated bottom. They may be obtained by special order from any dealer in chemical platinum.

The asbestos which we have found to give best results is the mineral known as "actinolite." We consider it essential to ignite the material as received after it has been picked up and cut with shears into short lengths, either in a platinum dish over a Bunsen burner, or in the combustion tube itself, in a current of oxygen. After a quantity of the ignited material has been prepared it should be mixed with water in a beaker and kept under cover as stock supply. To prepare the filter in the boat everything is put in position just as for a filtration and the suction started. The asbestos and water mixture, which should be pretty well diluted, is first stirred up well, in order to make some of it float, and then poured on the boat its whole length, taking care to have the asbestos evenly distributed. The suction re-

moves the water as fast as it is poured on and shows where to pour next. A filter about one-sixteenth inch thick seems to work very satisfactorily. It is usually not necessary to make a fresh filter after each combustion, especially if the copper is completely dissolved before filtration, and if proper care is taken to wash the carbon clean. Under these conditions the same filter may be used over and over again by simply scraping off a little of the top and freshening it up with a little of the asbestos and water mixture after each combustion.

The drying of the carbon on the filter may be done either in the well-known drying oven with hot water or in the drying oven with hot air. We use the latter with an automatic regulator on the gas supply to maintain constant temperature.

The combustion train is shown in Figure 3. Beginning at the left hand, first are two gas holders, one for oxygen gas and the other for air. These are simple copper gas holders with movable weights for pressure. They are adjusted so that the pressure will just cause the gas to bubble through the purifying potash bulb, next to the combustion furnace, but not cause it to pass through the bubble tube containing iron sulphate, just to the right of the combustion furnace. The connection between these gas holders and what we call the preheating furnace, is by means of rubber tubes, and a glass Y tube. These rubber tubes should, of course, be closed by a cock or clamp, so that gas can be taken from either without contamination from the other. The preheating furnace is, as will be observed, a simple twelve-inch Fletcher furnace, fitted with a porcelain combustion tube five-eighths inch in diameter and twenty inches long, which contains granulated oxide of copper for about eight or ten inches of its length inside the furnace. A second combustion furnace would do equally well for a preheating furnace. The corks used with this and also with the combustion furnace are rubber; also rubber tubes are used for connections. The placing of the porcelain tube in the preheating furnace should be such that not less than four or five inches of its length projects towards the combustion furnace, so that this end may not become heated, with consequent danger of volatilizing hydrocarbons from the rubber cork. Also to prevent overheating of the porcelain tube,

the gas holes in the gas tube of the preheating furnace are stopped up about two and one-half inches each way from the ends. Next beyond the preheating furnace is an ordinary Geissler potash bulb, which may be called the purifying potash bulb, properly filled with caustic potash solution, to retain any carbon dioxide that may be in the oxygen or air used, or that may be formed in the preheating furnace from the combustion of any vapors containing carbon in these gases. The connection between this potash bulb and the porcelain tube in the preheating furnace should be so arranged that the glass tubes, which are embraced with the rubber tube, should have square ends and should touch, so as to avoid exposure of the current of gas to the rubber tube as much as possible. This same remark applies to all other rubber tube connections. Next beyond the purifying potash bulb is the combustion furnace. The fourteen inch Bunsen furnace gives excellent results. We use coal gas for fuel. The combustion tube is royal Berlin porcelain, glazed inside and outside, five-eighths inch internal diameter, and twenty-four inches long. The tube should be placed symmetrically in the furnace, that is, should project five inches at each end. It should be prepared for use by placing a small plug of asbestos or three or four disks of copper gauze, which are large enough to fit tightly at a point six inches from the right hand end of the tube. Then put in granulated oxide of copper, followed by another asbestos plug or copper gauze disks for four and one-half inches toward the left hand end of the tube. Then make a roll of metallic silver foil, two inches long, rolled moderately closely, until it almost fills the bore of the tube, and place this next to the material already in the tube. This leaves abundant space in the tube for the boat, which should be pushed in so as to touch the silver roll. Next beyond the combustion tube is a bubble tube, not quite half full of acid ferrous sulphate solution, which serves to catch any free chlorine which may escape from the combustion tube, and next beyond this is a bubble tube, not quite half full of silver sulphate and water, which serves to catch any hydrochloric acid that may come out of the combustion tube, or from the ferrous sulphate bubble tube. The solubility of the silver sulphate being rather meagre, it is desirable to add some

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of the solid salt to the bubble tube in order to prevent the necessity of too frequent charging of this tube. Next beyond the silver sulphate bubble tube, is an ordinary chloride of calcium tube. In order to save space, we prefer the U form. Next is the absorption potash bulb. We prefer the Geissler form, and have them made so that when filled, they with the prolong, weigh from fifty to sixty grams. The ordinary size weigh from eighty to ninety grams. Next is the prolong, which is simply a small chloride of calcium tube filled with granulated chloride of calcium only. Next is another ordinary chloride of calcium tube to protect the prolong from moisture from the aspirator bottle. This bottle finishes the train. It is provided, as will be observed, with inlet at the top and side outlet at the bottom, which latter is also provided with glass tube of sufficient length to give the necessary suction, and a clamp on the rubber hose connection to regulate the flow.

The double chloride of copper and potassium solution is made by dissolving ten pounds of the commercial salt in thirteen liters of water, filtering through ignited asbestos, and adding one liter of concentrated C. P. hydrochloric acid (sp. gr. 1.20).

The caustic potash solution used both in the purifying potash bulb and the absorption potash bulb, is made by dissolving one pound of commercial stick caustic potash in a small amount of water, and then diluting until the resulting liquid when cold shows a sp. gr. of 1.27. A pound of potash makes about a quart of solution.

The granulated oxide of copper may be made by igniting the nitrate in a Hessian crucible until nitrous fumes cease to come off, but not fusing the material; or may be obtained in the market. If the ignition of the nitrate is properly conducted, a porous granular material is obtained, which gives very satisfactory results. Most of the material in the market has been fused and is very dense, and liable to contain impurities. We regard it essential, therefore, to place this fused material in the pre-heating and combustion tubes, as described, fitting them at the exit end with a small jet tube, then place in the furnace and reduce with hydrogen gas. It is essential during the reduction that the tube where the oxide of copper is, should be heated to

a full red heat, and in order to insure complete reduction, the gas should be passed for half an hour after it will burn at the jet. This being accomplished, allow the tube to cool and then replace the hydrogen with air, then heat up again, and pass oxygen gas until the reduced material is oxidized, which will take some time. The use of coal gas in place of hydrogen for the above reduction is admissible, provided the porcelain tube is heated two burners more each way, during the subsequent oxidation, than during the reduction in order to burn out any separated carbon that may have deposited in the tube.

The silver foil may be easily obtained in the market.

The acid ferrous sulphate solution is made by dissolving crystallized ferrous sulphate in water to nearly a saturated solution, and adding three or four drops of sulphuric acid to every fifty cc.

The sulphate of silver is made by precipitating nitrate of silver with carbonate of soda. Filter and wash thoroughly. Then place the precipitate in the vessel in which it is designed to keep the salt with a little water, and then add sulphuric acid at last, drop by drop, with thorough agitation, until all the carbonate is decomposed and the liquid is clearly acid to test paper. In filling the bubble tube shake the vessel and pour in enough of the milk to have one-fourth inch of the solid salt in the bottom when it has settled, and then fill the bubble tube about half full of water. If care is taken to wash the carbon in the boat thoroughly, once filling of the sulphate of silver bubble tube will be sufficient for thirty or forty combustions. Sulphate of silver may be obtained in the market, but we have no experience with this material.

The granulated chloride of calcium used in the chloride of calcium tubes and prolong is obtained in the market. We use the grade marked C. P., and like to have it as free as possible from other substances. The size we prefer is what will pass through holes about a tenth of an inch square and not pass through holes a twentieth of an inch square. Before filling the chloride of calcium tubes it is essential to dry the material, best in a platinum dish over a Bunsen burner for twenty minutes or half an hour, taking care, however, not to fuse it. Of

course the chloride of calcium used should not be alkaline, but for fear that it will be sufficiently so to absorb carbon dioxide, even if not sufficiently so to show by test, it is recommended to pass dry carbon dioxide into each freshly filled chloride of calcium tube and allow it to remain over night, and then replace with dry air, before using such tubes in actual work.

The oxygen gas used may be obtained in the market in cylinders compressed to almost any desired pressure. We transfer to the small gas holders shown in the cut, rather than take the gas direct from the cylinders, since the gas holders can be adjusted to give uniform pressure in the tube. This commercial material may be contaminated by oil or vapors containing carbon from the pump used in compressing it, and we accordingly deem it essential to pass it through the preheating tube as described before it goes into the combustion furnace.

After the combustion train is arranged as above described, it is essential to see that there are no leakages, and to make not less than two blank combustions. For the first of these, close the connection from the gas and air holders, and then open the cock controlling the flow from the aspirator bottle, which has been previously filled with water. This puts suction of a column of water twelve to eighteen inches high on the train, and is abundant to indicate any leaks. After the suction has had time to act on the whole apparatus and come to rest, it is satisfactory if nothing passes the absorption potash bulb for five minutes. If this result does not follow, the leaks must of course be found and stopped. The combustion train being found tight, the two blank combustions should be made in every respect as though they were real ones, except of course no iron or steel should be put in the dissolving jar. If these blanks change the weight of the absorption potash bulb and prolong more than about one milligram, something is wrong, and the apparatus and chemicals should not be regarded as satisfactory until one or more blanks are obtained which come within the limit above mentioned. In this connection the paragraph below on necessary errors should be read.

#### CALCULATIONS.

Since the carbon is weighed as carbon dioxide, and since

three-elevenths of the carbon dioxide is carbon, the percentage of carbon in the iron or steel under test may always be found by the following formula,  $a:100::\frac{8}{11}b:x$ , in which  $a$  represents the amount of iron or steel taken, expressed in grams;  $b$  the increase in weight of the absorption potash bulb and prolong expressed likewise in grams; and  $x$  the carbon sought. This proportion reduces to the form  $x=300b\div11a$ , and when three grams are used to start with, it becomes  $x=100b\div11$ . When three grams are taken to start with, this may be briefly stated as follows: Express the increase in weight of the absorption potash bulb and prolong in grams, move the decimal point two places to the right, and divide by 11. The result will be the percentage of carbon in the sample. Thus if the increase in weight is 0.1661 gram, the carbon will be  $(16.61\div11)$  1.51 per cent.

#### NOTES AND PRECAUTIONS.

It will be observed that this method releases the carbon from the iron or steel by dissolving the metal in an acid solution of the double chloride of copper and potassium, and after filtration and thorough washing burns the carbon in a tube in oxygen gas, and after freeing the carbon dioxide formed from impurities, catches it in caustic potash solution, the amount being determined by the increase in weight of the absorbing material.

There is much reason to believe that many discrepancies in duplicate analyses, as well as between different chemists, are due to the borings or drillings. The place from which the drillings are taken; the size of the drill; the depth of the hole; whether it goes through the sample or not, and especially whether the drillings are partly coarse and partly fine, are all believed to have considerable influence on the final result. This difficulty will be diminished (1) by drilling the hole as near through the sample as practicable; (2) by having this hole transverse to the line of final solidification, and cutting it, and (3) by having the drillings as fine as possible, and thoroughly mixing them. This latter precaution, *viz.*, to have the drillings fine, is also important in its influence on the rapidity of subsequent work.

The use of acid and the use of the potash double salt, rather

than the ammonium double salt to dissolve the metal, both of which differ from old practice, are copied from the work of the American Committee on International Standards for the Analysis of Iron and Steel. It will be remembered that the work of this committee seemed to show very conclusively that these changes lead to much more accurate results.

If the solution contains more of the double salt than is recommended above, solution will not be so rapid. A saturated solution works very slowly.

The influence of stirring on the rapidity and completeness of solution is very great. With the stirring apparatus recommended above, if the borings are fine it is not at all rare, especially in the case of steels, to get such complete solution in fifteen to twenty minutes that but little more than a stain is left on the asbestos filter in the boat, after the combustion is finished. The reason why stirring is essential will be readily understood. Without stirring, that part of the liquid in immediate contact with the borings which reacts at once is soon used up, leaving the borings surrounded with either a neutral, or an acid liquid containing no active copper salt. Neither of these conditions is favorable to accurate results.

In washing the carbon in the boat, after it is transferred from the beaker or dissolving jar, loss of substance is apt to result, if the jet from the wash bottle is used direct. It is better to always put the liquids into the beaker or dissolving jar, and then pour them into the boat. Too great care can hardly be taken to wash thoroughly. A little sub-chloride of copper or a little chloride of iron left in the asbestos filter, or in the boat, may cause difficulty in the combustion tube later on.

The carbon from some steels, and in general from pig iron, filters readily like sand, but from other steels it seems to separate in such a form as to clog the filters badly. This gelatinous carbon does not seem to be characteristic of any special kind of steel, but may occur in any. We know of no way to facilitate filtration in such cases, except to follow the directions closely.

In drying the carbon in the boat, too high temperatures should be avoided. There are indications that loss of substance



may result from neglect of this precaution, although we have not positively demonstrated this.

The use of the preheating furnace complicates the train somewhat, but no other method of freeing the oxygen gas from possible injurious impurities has proven so successful in our experience as this one. It is clear that if there is anything in the gas that would react with oxygen or with oxide of copper in a red hot tube, and later be absorbed by caustic potash, this material must be removed from the gas by the preheating furnace and purifying potash bulb, before the gas goes into the combustion tube. Purifying the oxygen gas without preheating does not seem so satisfactory.

The use of rubber corks and rubber tubes is open to some objection, but we do not know of any successful substitutes for these materials.

The combustion tube we recommend is longer than customary, but we think not longer than essential. The danger of volatile matter from corks affecting the result is considerably diminished by this additional length. We prefer the porcelain tube, although we have never used platinum ones. Tubes of larger bore enable a little larger boat to be used, but they are much slower to heat, and do not in our experience give any more reliable results.

The use of a roll of fine copper gauze in the combustion tube in place of granulated oxide of copper has been recommended. In our experience, it is difficult to be sure that the metallic copper is all oxidized before regular work is begun. If this is not so, and if the metallic copper contains any carbon, there would, of course, be danger of error, due to the slow progressive oxidation of the metal and carbon during combustion.

Many devices have been suggested to prevent the possibility of hydrochloric acid, chlorine or chlorine compounds, which may be formed in the tube during combustion from reaching the absorption potash bulb, and thus introducing error. We have tried many that we have seen suggested, but have found none that seem so efficient as the roll of metallic silver foil. If proper care is taken in the washing of the carbon, if the tube is arranged as described and in good order, and if the rate of

movement of the gases is not too rapid, neither chlorine nor hydrochloric acid escapes from the tube. If, however, the washing is incomplete, leaving some sub-chloride of copper or ferrous chloride and free hydrochloric acid in the boat, which latter is not expelled by the drying; if the tube is foul from having been used for many combustions, without cleaning and recharging, or reduction by hydrogen, and especially if the combustion is hurried, resulting in a too rapid movement of the gases in the tube, the silver roll may not be a complete protection. We accordingly introduce into the train an acid ferrous sulphate, and a silver sulphate bubble tube as additional precaution, the former to catch chlorine, and the latter hydrochloric acid. Direct experiments with each of these tubes separately show that they are a complete protection against the gases mentioned, provided the rate of movement is not more than four or five bubbles a second, and also provided the amount of these gases is not greater than would arise in even the rather carelessly managed combustion mentioned above. Of course it may be questioned whether these two bubble tubes do not retain carbon dioxide and thus cause error. Direct experiments made by taking a weighed potash bulb and prolong, properly filled with water, protecting it with chloride of calcium tubes at each end, and charging it full of carbon dioxide, and re-weighing and then aspirating air through it with frequent weights during the aspiration show that a very much less amount of air than that used for aspiration in a regular combustion, is sufficient to remove the carbon dioxide completely from the amount of liquid in the bubble tubes.

It is highly desirable to pass hydrogen or coal gas, preferably the former, through the combustion tube, as described above, after a tube has been used for fifty or sixty combustions. In lieu of this, the tube should occasionally be cleaned out and filled with fresh material. The frequency with which either of these should be done, depends largely on how completely the carbon is freed from other substances during the solution, washing, and drying.

A slight pressure in the tube is thought to be less liable to lead to error from leakages than to have a vacuum in the tube,

caused by drawing everything through the train by means of the aspirator bottle. It will be observed that the pressure specified is equal to about half the column of water in the first bubble tube. From this point the aspirator bottle is relied on to move the gases forward.

The combustion tube should always be kept closed, and after a combustion is finished, the connection between the air, gas holder, and the train should be left open, or the liquid in the bubble tubes will suck back into the combustion tube as it cools. We also deem it essential after the furnace has been standing idle some time, to make a blank before proceeding with regular work in order to be sure that everything is right.

It is quite essential that the chloride of calcium tube which precedes the absorption potash bulb and the prolong should dry the gases to the same extent and no more. If one is more efficient than the other, error may result. Thus if the gases which go into the absorption potash bulb, are drier than they are after they leave the prolong, it is obvious that moisture that has been weighed is lost. On the other hand, if the gases that go into the absorption potash bulb are not as dry as when they leave the prolong, it is equally obvious that something besides carbon dioxide has increased the weight of the absorption potash bulb and prolong. It seems probable that some of the difficulty in getting absolute blanks may be accounted for in this way. It is a little hazardous to use a freshly filled chloride of calcium tube with an old prolong, and vice versa. Likewise it is not advisable to use sulphuric acid or other means of drying the gases between the furnace and the chloride of calcium tube.

It is not necessary to recharge the absorption potash bulb for each combustion. Depending of course on the amount of carbon in the sample, they may be used for from three to six or eight combustions without recharging. We have made agreeing duplicates on the same sample, one with a potash bulb, freshly charged, and the other with a potash bulb showing a cloudiness in the first bulb due to bicarbonate.

The weight of the potash bulb and prolong before and after the combustion, is affected by a number of circumstances, other than the carbon dioxide absorbed. It is obvious that if all the

conditions are the same at the second weight, which prevailed at the first, there is no error due to weighing. But it seems to be difficult to get these conditions exactly the same. Temperature, barometric pressure, the deposit of something from the air of the laboratory, or from the fingers on the parts weighed, and especially the humidity of the air, may all be different at the second weighing than at first. If we may trust our experience, it is almost impossible to make satisfactory combustions in showery weather.


Where combustions are made in large numbers, say sixteen to eighteen a day, by one operator, with two furnaces, very satisfactory results may be obtained by weighing direct from the furnace, finishing the aspiration with oxygen, instead of air, and using the last weight of one combustion as the first weight of the next one. Of course in arbitration work, this would hardly be satisfactory.

Direct experiments show that with the apparatus arranged as above, the oxygen in the potash bulb and prolong is all removed by air during aspiration, when about 800 cc. of water has been run out of the aspirator bottle. The experiments were made by weighing a potash bulb and prolong, introducing it in the train, passing oxygen until it was filled, then reweighing, and then aspirating air with frequent weighings until the first weight was obtained.

If the aspirator bottle is fitted with a tube reaching nearly to the bottom as shown, the suction on the train will be the same irrespective of the amount of water in the bottle, until the bottom of the tube is reached.

Notwithstanding all precautions, there seem to be some almost unavoidable sources of error in the combustion method of determining carbon. Among these may be mentioned the possibility of hydrocarbon vapors from the rubber tubes and corks, the unequal drying of the gases by the chloride of calcium tube and prolong, the difficulty of getting absolute blanks, and especially the difficulty of making the second weight, under exactly the same conditions as prevailed when the first one was made. We do not think all these errors combined should amount to more than one or two hundredths of a per cent. of carbon.

[NOTE.—Dr. Dudley informs the editor that the methods for sulphur in steel and sulphur in pig and wrought iron are nearly ready for publication.]



## MODELS FOR ILLUSTRATING THE RELATIONSHIP BETWEEN GAS VOLUMES AND MOLECULAR WEIGHTS<sup>1</sup>.

BY W. SIMON.

Received October 4, 1893.

THE difficulty experienced by students in fully comprehending the laws of Gay Lussac, and the hypothesis of Avogadro, has led the author to the use of object lessons in his lectures. The particular models herein described are intended to represent atoms and molecules, each atom possessing a definite weight, but a changeable volume. By means of these may be illustrated the alterations which occur in the volume of gases when they undergo chemical change; as well as the relations existing among those volumes, and among their molecular weights.

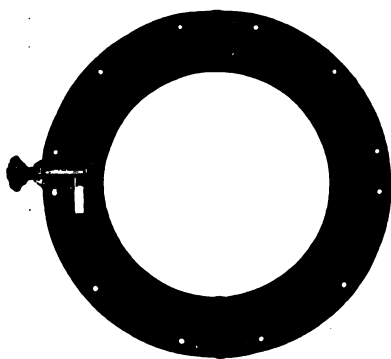


FIGURE 1.



FIGURE 2.

The models may be described as follows:—

To a circular metallic frame (Fig. 1) of five centimeters diameter, formed of two semi-circular pieces joined by hinges, is fastened a hemisphere of cloth or leather, arranged in folds like an accordion bellows. The frames are provided with locks which permit the joining together of two (or more) hemispheres, as shown in Fig. 2. Two or more hemispheres form a spherical molecule. By using various materials in constructing the frames, the hemispheres are made to correspond to the atomic

<sup>1</sup> Abstract of a paper read before the educational section of the American Pharmaceutical Association, Chicago meeting, August, '93.

weights of the different elements, which latter a characteristic color serves to distinguish. Thus, a black hemisphere, representing carbon, weighs twelve times as much, and a green one representing chlorine thirty-five times as much, as a pale blue hydrogen hemisphere.

To illustrate the changes which take place when hydrogen and oxygen combine to form water:—Two glass cylinders of five cm. diameter and twenty cm. high are filled with hydrogen molecules, and a like cylinder is filled with oxygen molecules. The condensation to two volumes is effected by joining an oxygen atom to each two atoms of hydrogen, forming a spherical molecule of water. The volumes should be weighed before and after condensation.

The writer begs to remind teachers that the use of the models should always be accompanied by an experiment with the gases themselves, and also to recall the necessity of impressing upon students the fact that the models are intended only to represent pictures (however distorted) of our conceptions of some chemical changes; and that they are not magnified illustrations of actual atoms and molecules.

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#### NOTES.

*A Mineral Group from York, Pa.*—In the same quarry from which fluorite was reported,<sup>1</sup> the writer recently found a group of four minerals, namely, fluorite, calcite, pyrite, and dolomite, all except fluorite showing very perfect crystals. The fluorite is imbedded in calcite and dolomite which are closely intermingled. The crystals of calcite are the common prisms with rhombohedral terminations, the length and thickness being about equal. Others are thin, tabular in form. They vary in size up to an inch or more in diameter. The pyrite occurs on the surface of the dolomite and consists of perfect little cubes, scarcely more than one-half mm. square. Their surface is brown owing to oxidation.

As the dolomite has not to my knowledge been heretofore reported from this locality it is noticed a little more fully. It is

<sup>1</sup> See *J. Anal. Chem.*, July, 1890.



the Pearl-spar variety. The crystals occur not only distinct on the surface of the rock, but are often so massed together as to form veins  $\frac{1}{4}$  inch thick in the limestone. It has a beautiful pink color. The crystals are the common curved-face rhombohedra with pearly luster, the largest being about  $\frac{1}{4}$  inch across. Sp. gr. = 2.81.

An analysis gave the following results:

	Per cent.
CaO.....	32.04
MgO.....	20.09
FeO.....	1.18
Al <sub>2</sub> O <sub>3</sub> .....	0.38
CO <sub>2</sub> .....	45.91
	<hr/> 99.60
	C. H. EHRENFELD.

### NEW BOOKS.

FOUNDATIONS OF THE ATOMIC THEORY. PAPERS, ETC., BY JOHN DALTON, WILLIAM HYDE WOLLASTON, M.D., THOMAS THOMSON, M.D. 1802-1808. Alembic Club Reprints, No. 2. 12mo. 48 pp. Wm. F. Clay.

This number contains two papers by Dalton taken from the Memoirs of the Literary and Philosophical Society of Manchester; the first, an "Experimental Inquiry into the Proportion of the Several Gases or Elastic Fluids Constituting the Atmosphere;" the second, "On the Absorption of Gases by Water and Other Liquids." At the end of his second paper is given the famous first table of atomic weights. These papers are followed by two extracts from Dalton's New System of Chemical Philosophy, and then follow a paper from the Philosophical Transactions by Wollaston on "Super-Acid and Sub-Acid Salts," extracts from a paper on oxalic acid by Dr. Thomson, also from the Philosophical Transactions, and an extract from Thomson's "System of Chemistry" containing the account of Dalton's Hypothesis.

E. H.

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### OPENING ADDRESS.

SECTION OF TECHNICAL CHEMISTRY.<sup>1</sup>

BY WM. MCMURTRIE.

**I**T is my honored privilege and very pleasant duty to call to order the Section of Technical Chemistry at the World's Congress of Chemists, and in doing so I cannot refrain from expressing my personal satisfaction, in the numerous responses to the call for it and the generous list of subjects we shall be able to discuss.

Of the importance of the work being done by the technologists in this and other countries for the advancement of the great science we represent and for its applications to the varied uses of mankind, little need be said before such an audience as this. It has truly been said in this room that the practical applications of the principles of the science have been the forerunners of the development of these principles themselves; and the necessities which these applications have involved, have indeed led to that deeper search for knowledge and to the stimulation of that faculty of invention through which and by which such development of principles could alone be possible. As man's necessities have increased, the development of the great principles which govern all our work has grown, and greatness in both these lines of human activity has been achieved by reciprocal reaction and mutual aid. In the earlier years of the history of our science, the technologists, the toilers in the works

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893.



and factories of the manufacturers, depended largely and almost wholly upon the laboratories independently devoted to research, for the closer knowledge of the empirical methods they were forced to employ; but stern necessity, brought about by commercial competition and trade requirements has caused a closer union between the manufacturer and the analytical chemists, and to-day few successful works will be found in this or any other country in which competent corps of analytical and research chemists are not firmly established, controlling laboratories in which the additions to the sum of human knowledge are being massed in mountains of experience and progress. It is true that much of this knowledge is being immediately applied to what seems to be more or less selfish ends. But in this as in other lines, brilliant light cannot be forever hid, and the discoveries and advances here made soon show themselves, first in the new products, then in the extended works, and finally through the stimulus of necessity aroused in others in greater discoveries elsewhere. Truth once developed and brought forth cannot long be kept back, and it is therefore fair to say that the work of the chemists in the technical lines is doing as much to develop the science we all love so much, as the work of that noble and unselfish class who so earnestly struggle after the more abstract principles. The advancement that is being thus made is reflected fairly well in the list of the patented inventions, and the statistics. In the class of chemicals alone, there have been issued from the American patent office during the past decade patents for 657 such inventions. And when we reflect upon the restrictions which from year to year increasingly bear upon the issue of all letters patent we must see in this record, indications of much earnest thought and patient work.

If we consider the value of the product of the applications of chemistry in the arts we must be impressed more than ever by the importance of the work entrusted to those who constitute the section I have had the honor to call to order. Statistics collated by competent authority, as will appear in one of the papers that will be presented in this section, will show that the value of these products reached in 1890 the enormous addition

to our national wealth of \$176,000,000. Such data are significant and are a just source of proper pride to those engaged in the work of production.

It has seemed to me that no time or place could be more auspicious for this International Congress of Chemists called to discuss the advances that have lately been made and the possibilities for the future. If we look to the immediate past we see that the advances that have been made during the past three or four years have all the importance of the work of a decade, and whether we look to the organic side of the work or over the inorganic field we see the same enormous activity. In the dyes so rich and so beautiful, in the explosives so powerful and terrible, in the valued additions to our materia medica continual evidence of progress is manifest; in metallurgy the minute exactness in extraction of the precious metals from very low grade ores illustrated in the cyanide process for gold and its modifications and the aluminum zinc process for desilverization of lead—the oxidation and basic process for extraction of copper, the electrolytic processes for extraction and purification of this metal, the new and beautiful process of Mond for extraction of nickel through the production of its carbonyl compound, the extension of the value of aluminum by increase of its strength through the inventions of Prof. Langley must all challenge our ardent admiration and our most profound respect, while the addition to our resources in the new and developing processes for the production of the alkaline products and the bleaching agents and the chlorates by the application of electrolysis and the economies effected thereby all show profundity of research and keenness of invention rarely if ever witnessed in industrial work. Added to these are the condensation of chlorine and its delivery in liquid form, the production of phosphorus by electrolysis with increased economy and diminished danger over the old reduction processes, and the beautiful methods and apparatus for the production of pure oxygen from the atmosphere at substantial reduction of cost. All these advances following each other with such remarkable rapidity become footprints in the path of progress as lasting as they are deep.

In this city of our temporary adoption, in which are to be

found many of the industries managed on a scale only to be dreamed of in the earlier years, we must find splendid inspiration for future work. It is perhaps fair to say that nowhere else in the world can be found so extensive operations in the production of animal fats and oils; in the complete utilization of the waste animal products; in the manufacture of crude fertilizers, glue, soap, and glycerol; in the manufacture of malt, spirits, and the products of brewing, glucose and refined sugar. These are some of the products of technical work common to the city and while such a list must of necessity be incomplete it is sufficient to amply illustrate the sympathy with our work to be found in our immediate surroundings.

And within easy reach as we are of the great exhibitions of the products of chemical manufactures, those signs of the world's progress resulting from the efforts in which most of us are engaged, we must easily find valued causes for earnest congratulation.

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### THE TECHNICAL ESTIMATION OF LEAD.

BY ALBERT H. LOW.

Received October 30, 1893.

THE ordinary fire assay for lead in ores is frequently so erroneous in its results as to cause great dissatisfaction. With some ores the results are considerably too low, and with others, notably oxidized ores containing iron or copper, the lead button may contain several per cent. of such impurities, and weigh more than is warranted by analysis. In Colorado there has been considerable agitation in favor of abandoning the fire assay for a wet method, but thus far no concerted action has resulted. One of the main objections to a wet method is the lack of a suitable one. A number of schemes, both gravimetric and volumetric, have been proposed, but they all appear to be either too lengthy and troublesome or too inaccurate. The writer has devoted much of his spare time to the subject, and feels that the ideal method has not yet been evolved. Alexander's molybdate method is the shortest scheme proposed, but, unfortunately, lime interferes, and lime is a common constituent of ores. The writer's ferrocyanide method, described below, might

be made equally short if the question of lime were neglected. To be sure, the small percentage of lime found in perhaps the majority of the ores might with safety be neglected, on account of the solubility of its sulphate and consequent removal, but it would appear dangerous to employ a method in which lime might seriously interfere, as almost any attempt to remove much lime would also remove some lead. In the two following schemes, devised by the writer, almost any ore may be treated with safety with results that are quite accurate enough for technical work. The first method is based upon the writer's gravimetric method and Hempel's titration of the oxalate. In the second method the titration with ferrocyanide is apparently new. Both methods are of course susceptible of slight modifications in special cases and appear to give equally accurate results. The ferrocyanide method is considerably the shorter, but on the other hand the titration with permanganate is more rapid and satisfactory than where the tests have to be made on a plate. The methods are given for what they are worth as an addition to the literature on the subject.

#### PERMANGANATE METHOD.

Treat one gram of ore in a 250 cc. flask with about 10 cc. of aqua regia. Boil gently until decomposition appears about complete and then add 10 cc. of strong sulphuric acid and heat over a small naked flame until the sulphuric acid fumes are freely evolved. Cool and add 50 cc. of water and heat to boiling. Filter through a small filter and wash with dilute sulphuric acid, (1 : 10). Have boiling in a wash bottle a solution of commercial ammonium chloride, made by diluting a cold saturated solution with an equal bulk of water. Spread the filter upon a watch-glass, and with the hot ammonium chloride solution, rinse the contents into a small beaker, using about 50 cc. of the chloride solution. Stir the mixture to dissolve as much of the sulphate of lead as possible and decant the solution into the original flask, retaining any heavy residue in the beaker. This residue may contain lead. Add to it a few cc. of a strong solution of caustic soda and heat to boiling. Any lead salts will quickly dissolve. To this solution add sufficient dilute sulphuric acid to cause a precipitation of the lead, or

most of it, avoiding an excess, and rinse the contents of the beaker into the flask with the hot chloride solution. A failure of the sulphate of lead to redissolve is of no consequence. Place in the flask three pieces of sheet aluminum, each about one-sixteenth of an inch thick by five-eighths of an inch wide and an inch and three-quarters long. Commercial aluminum will answer. Heat the mixture to boiling and boil for five minutes. If the bulk of the solution is not too great the lead will now be all precipitated. Now nearly fill the flask with cold tap water, allow the lead to settle and then decant into a large dish in order that any escaping particles of lead may be observed and recovered. Fill up and decant five times to remove the chlorides. Finally, to the lead and aluminum in the flask add 5 cc. of a mixture of one part strong nitric acid and two parts distilled water and warm gently. The lead easily dissolves. Pour the solution into a small beaker and shake the pieces of aluminum along with it. Rinse off merely the lip of the flask and then wash the solution back into it, retaining the aluminum in the beaker. To the solution add one or two drops of phenolphthalein solution and then a very slight excess of strong caustic soda solution. Now add 10 cc. of a cold saturated solution of oxalic acid and cool the mixture if warm. Filter and wash thoroughly with cold water. Place in the flask about 75 cc. of distilled water and add a few cc. of strong sulphuric acid. Have this heating while the oxalate of lead is being washed. Finally drop the filter and contents into the hot solution and titrate at once with permanganate solution of the same strength used for iron, *i. e.*, about one-tenth normal. The factor for iron multiplied by 1.888 gives the factor for lead. This figure is empirical and had best be determined by each operator for himself by dissolving 0.30 to 0.40 gram of pure lead, reduced from the acetate, in dilute nitric acid, (two water to one acid), and putting this through the entire process.

None of the ordinary constituents of the ores interfere with this method. The results are accurate within one or two-tenths of a per cent.

#### FERROCYANIDE METHOD.

Treat one gram of ore in a 250 cc. flask with about ten cc. of

aqua regia. Boil gently until decomposition appears complete and then add ten cc. of strong sulphuric acid and heat over a small naked flame until the sulphuric acid fumes are freely evolved. Cool and add fifty cc. of water and heat to boiling. Filter and wash with cold water. See that the filter is well creased so as to lie as flat as possible and prevent solid matter from getting under the fold. Place a funnel in the original flask and rinse the contents of the filter (without removing it from its funnel) into it as thoroughly as possible with cold water. Not more than fifty cc. of water need be used. Add ten cc. of a cold saturated solution of commercial carbonate of ammonium and heat to boiling,—the heating being necessary to ensure the complete conversion of any sulphate of calcium to carbonate. Cool to ordinary temperature, under the tap or otherwise, and filter through the original filter, washing flask and precipitate thoroughly with cold distilled water. Place in the flask some dilute acetic acid, equivalent to about five cc. of glacial acid and twenty-five cc. distilled water, and have it heating while the filter is being washed. The flask usually contains a small residue of lead carbonate which is thus recovered. Place the filter and contents in a large clean beaker and add the boiling hot acetic acid. Stir the mixture about until the carbonates are entirely dissolved, heating if necessary. Dilute with about 100 cc. of cold distilled water and the solution is ready for titration with standard potassium ferrocyanide. The end point is indicated by the usual brown tinge when a drop is tested on a porcelain plate with a drop of a saturated neutral solution of uranium acetate. Reserve a portion of the solution and titrate the main body rapidly until the end point is passed, then add most of the reserved portion and again titrate with more caution till the end is again passed. Finally rinse in the balance of the reserve and finish the titration two drops at a time, stirring well after each addition. When the final brown tinge is thus obtained allow a little time for the previous tests to develop and then deduct from the reading of the burette two more drops than are indicated by the tests, as a solution containing no lead shows the test only after the addition of the third drop of ferrocyanide. The standard ferrocyanide should

contain about ten grams to the liter. On the basis of one gram of ore taken for assay, one cc. of this solution will equal about one per cent. of lead. It is standardized on about 0.30 to 0.40 gram of pure lead, reduced from the acetate. This is dissolved in a little dilute nitric acid, (two water to one acid), then boiled with ten cc. of sulphuric acid and put through the entire process.

An ore may be assayed in thirty minutes by the above method.

While the above method answers in ordinary cases, to provide against bismuth and antimony (of which the basic sulphates might cause trouble), the following modification may be adopted: To the sufficiently cool residue of the sulphuric acid evaporation add ten cc. of dilute sulphuric acid, (1 : 10), and about two grams of Rochelle salt. When this is dissolved add forty cc. of water, heat to boiling and proceed as usual.

Lime interferes with this method only by a solvent action exercised by the acetate on the brown uranium ferrocyanide of the test. Thirty per cent. of lime in an ore, however, occasions no serious interference. Calcium sulphate must not be allowed in the acetate solution as it would cause a loss of lead as sulphate.

OCTOBER 25, 1893.

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## THE GELATINE EXPLOSIVES.

BY P. GERALD SANFORD, F. I. C., F. C. S.

Received October 5, 1893.

**A**MONG the various forms of explosives the material known as gelatine is one of the most important, and is rapidly displacing the older forms of dynamite. The gelatine explosives chiefly in use are known under the names of blasting gelatine, gelatine-dynamite, and gelignite. They all consist of the variety of nitro-cellulose known as collodion-cotton (*i. e.*, the penta and tetra-nitrates, the hexa-nitro-cellulose being known as gun-cotton) dissolved in nitroglycerol, and made up with various proportions of wood pulp, and some nitrate, or other material of a similar nature. Blasting gelatine consists of collodion-cotton and nitroglycerol without any other substance and was patented by Nobel in 1875. It is a clear, semi-transparent, jelly-like substance, of a specific gravity of 1.5 to 1.55,

slightly elastic, resembling India-rubber, and generally consists of ninety-two per cent. to ninety-three per cent. of nitroglycerol and seven per cent. to eight per cent. of nitro-cotton. The cotton from which it is made should be of good quality; the following is the analysis of a sample of nitro-cellulose which made very good gelatine:

	Per cent.
Soluble cotton.....	99.118
Gun-cotton .....	0.642
Non-nitrated cotton .....	0.240
Nitrogen .....	11.64
Total ash.....	0.25

The soluble cotton, which is a mixture of tetra and penta-nitro-cellulose,  $C_{12}H_{11}(ONO_2)_4$ , is soluble in ether-alcohol, in acetone, and in nitroglycerol; the hexa-nitro-cellulose or gun-cotton,  $C_{12}H_7O_4(ONO_2)_6$ , on the other hand is not soluble in nitroglycerol, or in ether-alcohol, but is soluble in acetone,<sup>1</sup> or acetic ether.

It is very essential, therefore, that the nitro-cotton used in the manufacture of the gelatine compounds should be as free as possible from gun-cotton, otherwise little lumps of undissolved nitro-cotton will be left in the finished gelatine. The non-nitrated or unconverted cotton should also be very low, in fact, considerably under a half per cent. The cotton before being used should always be tested by the government heat test, because if the cotton used does not stand this test the gelatine made with it can hardly be expected to do so. The cotton most suitable for gelatine making is that which has been finely pulped. If it is not already fine enough it must be passed through a fine brass wire sieve. It will be found that it requires to be rubbed through by hand and will not go through at all if in the least degree damp. The percentage of nitrogen in the nitrated cotton should be over eleven per cent.; it should be as free as possible from sand or grit, and should give but little ash upon ignition, not more than 0.25 per cent. The cotton, which is generally packed wet in zinc lined wooden boxes,

<sup>1</sup>The smokeless powder, "cordite," contains thirty-seven per cent. of gun-cotton dissolved in fifty-eight per cent. of nitroglycerol. This gun-cotton is first dissolved in acetone before admixture with the nitroglycerol.



will require to be dried, as it is very essential indeed that none of the materials used in the manufacture of gelatine should contain more than the slightest trace of water; if they do, the gelatine subsequently made from them will most certainly exude, and become both dangerous and comparatively useless. In order to find out how long any sample of cotton requires to be dried, a sample should be taken from the center of several boxes, well mixed, and about 1,000 grams spread out on a paper tray, weighed, and the whole then placed in the water oven at 100° C. and dried for an hour or so, and again weighed and the percentage of moisture calculated from the loss in weight; this will be a guide to the time that the cotton will probably require to be in the drying house; samples generally contain from twenty to thirty per cent. After drying for a period of forty-eight hours, a sample should be again dried in the oven at 100° C. and the moisture determined and so on, at intervals, until the bulk of the cotton is found to be dry, *i. e.*, to contain from 0.25 to 0.5 per cent. of moisture. It is then ready to be sifted; during the process of removing to the sifting house and the sifting itself, the cotton should be exposed to the air as little as possible, as dry nitro-cotton absorbs about two per cent. of moisture from the air at ordinary temperatures. The drying house usually consists of a wooden building, the inside of which is fitted with shelves, or rather framework, to contain drawers, made of wood with brass or copper wire netting bottoms. A current of hot air is made to pass through the shelves, and over the surface of the cotton, which is spread out upon them to the depth of about two inches. This current of air can be obtained in any way that may be found convenient, such as by means of a fan, or Roots blower, the air being passed over hot bricks or hot water pipes before entering the building. The cotton should also be occasionally turned over by hand in order that a fresh surface may continually be exposed to the action of the hot air; the building itself may be heated by means of hot water pipes, but on no account should any of the pipes be exposed; they should all be most carefully covered over with woodwork because when the dry nitro-cotton is moved, as in turning it over, very fine particles get into the air, and gradually settling on the pipes,

(window ledges, etc.) may become very hot, when the slightest friction might cause an explosion. It is on this account that this house should be very carefully swept out every day; it is also very desirable that the floor of this house should be covered with oil cloth or linoleum, as being soft it lessens the friction. List shoes should always be worn in this building, and a thermometer hung up somewhere about the center of the house, and one should also be kept in one of the trays to give the temperature of the cotton (especially the bottom of the tray), the one nearest to the hot air inlet should be selected; if the temperature of the house is kept at about  $40^{\circ}\text{C}$ . it will be quite high enough. The building must of course be properly ventilated, and it will be found very useful to have the walls made double, and the intervening space filled with cinders, and the roof covered with felt, as this helps to prevent the loss of heat through radiation, and to preserve a uniform temperature, which is very desirable. The dry cotton thus obtained, if not already fine enough should be sifted through a brass sieve, and packed away ready for use in zinc air-tight cases, or in India-rubber bags.

The various gelatine compounds, gelignite, gelatine-dynamite, and blasting gelatine, are manufactured in exactly the same way; the forms known as gelatine-dynamite differ from blasting gelatine in containing certain proportions of wood pulp and potassium nitrate, etc. The following are analyses of some typical samples of the three compounds:

	Gelatine.	Gelatine-dynamite.	Blasting gelatine.
Nitroglycerol .....	60.514	71.128	92.94
Nitro-cellulose.....	4.888	7.632	7.06
Wood pulp.....	7.178	4.259	....
Potassium nitrate .....	27.420	16.720	....
Water .....	.....	0.261	....
	<hr/> 100.000	<hr/> 100.000	<hr/> 100.000

The gelatine and gelatine-dynamite consists therefore of blasting gelatine, thickened up with a mixture of absorbing materials; although the blasting gelatine is weight for weight more powerful, it is more difficult to make than either of the

other two compounds, it being somewhat difficult to make it stand the exudation and melting test; the higher percentage of cotton too makes it expensive.

When the dry cotton, which has been carefully weighed out in the proportions necessary either for blasting gelatine or any of the other gelatine explosives, is brought to the gelatine making house, it is placed in a lead lined trough, and the necessary quantity of pure dry nitroglycerol poured upon it; the whole is then well stirred up, and kept at a temperature of from  $40^{\circ}$  to  $45^{\circ}$  C.; it should not be allowed to go much above  $40^{\circ}$  C. (but higher temperature may be used if the cotton is very obstinate and will not dissolve at  $40^{\circ}$  C.; great caution must, however, be observed in this case). The mixture should be constantly worked about by the workman with a wooden paddle for at least half an hour. At a temperature of  $40^{\circ}$ - $45^{\circ}$  the nitroglycerol acts upon the nitro-cotton and forms a jelly. Without heat the gelatinization is very imperfect indeed, and at temperatures under  $40^{\circ}$  C. takes place very slowly. The limit of temperature is  $50^{\circ}$  or thereabout; beyond this the jelly should never be allowed to go, and to  $50^{\circ}$  only under exceptional circumstances. The tank in which the jelly is made is double lined in order to allow of the passage of hot water between its inner and outer linings. A series of such tanks are generally built in a wooden frame work, and the double linings are made to communicate so that the hot water can flow from one to the other consecutively. The temperature of the water should be about  $60^{\circ}$  C. if it is intended to gelatinize at  $45^{\circ}$  and about  $80^{\circ}$  C. if at  $50^{\circ}$ , but this point must of course be found by experiment for the particular plant used. An arrangement should be made to enable the workman to at once cut off the supply of hot water and pass cold water through the tanks in case the explosive becomes too hot. The best way to keep the temperature of the water constant is to have a large tank of water raised upon a platform, some five or six feet high, outside the building, which is automatically supplied with water, and into which steam is turned. A thermometer stuck through a piece of cork and floated upon the surface of the tank will give the means of regulating the temperature. When the jelly

in the tanks has become semi-transparent and the cotton has entirely dissolved, the mixture should be transferred to a mixing machine. An ordinary bread-kneading machine does very well. It must, of course, be made of gun-metal. There must be no iron about the working parts, and the bearings must be carefully looked to. A very suitable masticating machine for this purpose is supplied by Messrs. Werner and Pfleiderer, of London, or G. McRoberts' machine may be used. This latter is the form of machine<sup>1</sup> that is used at Nobel's factories.

If it is intended to make gelignite, or gelatine-dynamite, it is at this point that the proper proportions of wood pulp and potassium nitrate should be added and the whole well mixed for at least half an hour until the various ingredients are thoroughly incorporated. These mixing machines can either be turned by hand or a shaft can be brought into the house and the machine worked by means of a belt at twenty to thirty revolutions per minute. The bearings should be kept constantly greased and examined, and the explosive mixture carefully excluded. When the gelatine mixture has been thoroughly incorporated and neither particles of nitrate or wood meal can be detected in the mass, it should be transferred to wooden boxes and carried away to the cartridge-making machines to be worked up into cartridges. The application of heat in the manufacture of jelly from collodion-cotton and nitroglycerol is absolutely necessary, unless some other solvent is used besides nitroglycerol, such as acetone, acetic ether, methyl or ethyl alcohol. These compounds not only dissolve the nitro-cellulose in the cold, but render the resulting gelatine compound less sensitive to concussion, and reduce its quickness of explosion. They also lower the temperature at which the nitroglycerol becomes congealed, *i. e.*, they lower the freezing point of the resulting gelatine. The finished gelatine upon entering the cartridge huts, is at once transferred to the cartridge-making machine, which is very like an ordinary sausage-making machine.<sup>2</sup> The whole thing must be made of gun metal, or brass, and it consists of a conical case containing a shaft and

<sup>1</sup> See *J. Soc. Chem. Ind.*, 1890, 267.

<sup>2</sup> G. McRoberts, *J. Soc. Chem. Ind.*, March 31, 1890, p. 266.

screw. The revolutions of the shaft causes the thread of the screw to push forward the gelatine introduced by the hopper, on the top to the nozzle, the apex of the cone-shaped case, from whence the gelatine issues as a continuous rope. The nozzle is of course of a diameter according to the size of cartridge required. The issuing gelatine can of course be cut off at any length. This is best done with a piece of wood planed down to a cutting edge, *i. e.*, wedge-shaped. It is also essential that the machines should have no metallic contacts inside. The bearings for the shaft must be fixed outside the cone containing the gelatine. One of these machines can convert from five to ten hundred-weight of gelatine into cartridges *per diem*, depending upon the diameter of the cartridges made. After being cut up into lengths of about three inches, the gelatine is rolled up in cartridge paper; water-proof paper is generally used. The cartridges are then packed away in card-board boxes, which are again packed in deal boxes lined with India-rubber and screwed down air-tight, brass screws, or zinc or brass nails being used for the purpose. These boxes are then ready for the magazines or export. Before the boxes are fastened down, a cartridge or so should be removed and tested by the government heat test, the liquefaction test, and the test for liability to exudation (as described in Appendix, p. 6, Explosives Act, 1875). A cartridge also should be stored in the magazine in case of any subsequent dispute after the bulk of the material has left the factory. The object of the liquefaction test is to insure that the gelatine shall be able to withstand a fairly high temperature without melting or running together. The test is carried out as follows: A cylinder of the gelatine is cut from the cartridge of a length equal to its diameter. The edges must be sharp. This cylinder is to be placed on end on a flat surface (such as paper), and secured by a pin through the center, and exposed for 144 consecutive hours to a temperature of 85°–90° F; and during such time the cylinder should not diminish in height by more than one-fourth inch, and the cut edges should remain sharp. There should also be no stain of nitroglycerol upon the paper. The exudation test consists in freezing and thawing the gelatine three times in succession.

Under these conditions there should be no exudation of nitroglycerol. All the materials used in the manufacture of gelatine explosives should be subjected to analytical examination before use, as success largely depends upon the purity of the raw materials.<sup>1</sup>

*Properties of the Gelatine Compounds.*—Blasting gelatine is generally composed of ninety-three to ninety-five parts nitroglycerol and five to seven parts of nitro-cellulose, but the relative proportions of explosive base and nitroglycerol, etc., in the various forms of gelatine compounds do not always correspond to those necessary for total combustion. Either because an incomplete combustion gives rise to a greater volume of gas, or because the rapidity of decomposition and the law of expansion vary according to the relative proportions and the conditions of application. The various additions to blasting gelatine generally have the effect of lowering the strength by reducing the amount of nitroglycerol, but this is sometimes done in order to change a shattering agent into a propulsive agent. If this process be carried too far we of course lose the advantages due to the presence of nitroglycerol. There is therefore a limit to these additions.<sup>2</sup> The homogeneousness and stability of the mixture are of the highest importance. It is highly essential that the nitroglycerol should be completely absorbed by the substances with which it is mixed, and that it should not subsequently exude when subjected to heat or damp. It is also important that there should be no excess of nitroglycerol, as this may diminish instead of augment the strength owing to a difference in the mode of the propagation of the explosive wave in the liquid and in the mixture. Nitroglycerol at its freezing point has a tendency to separate from its absorbing material, in fact, to exude. When frozen, too, it requires a more powerful detonator to explode it, but it is less sensitive to shock. The specific gravity of blasting gelatine is 1.5 (*i. e.*, nearly equal to that of nitroglycerol); that of gun-cotton (dry) 1.0. Blasting gelatine burns in the air when unconfined without explosion, at least in small quantities and when not previously heated; but

<sup>1</sup> For some of the chief methods in use, see *J. Anal. Appl. Chem.*, June, 1892.

<sup>2</sup> Mica is said to increase the rapidity of explosion when mixed with gelatine.

it is rather uncertain in this respect. It can be kept at a moderately high temperature ( $70^{\circ}$  C.) without decomposition. At higher temperatures the nitroglycerol will partially evaporate; when slowly heated it explodes at  $204^{\circ}$  C. If however it contains as much as ten per cent. of camphor it burns without exploding. According to Berthelot,<sup>1</sup> gelatine composed of 91.6 per cent. nitroglycerol and 8.4 per cent. of nitro-cellulose, which are proportions corresponding to total combustion, produces by explosion  $177\text{CO}_2 + 143\text{H}_2\text{O} + 8\text{N}_2$ .

He takes  $\text{C}_{12}\text{H}_{22}(\text{NO}_2)_3\text{O}_{11}$  as the formula of the nitro-cellulose, and  $51\text{C}_6\text{H}_7(\text{NO}_2)_3 + \text{C}_{12}\text{H}_{22}(\text{NO}_2)_3\text{O}_{11}$  as the formula of the gelatine itself, its equivalent weight being 12360 grams. The heat liberated by its explosion is equal to 19381 calories, or for one kilo., 1535 calories, volume of gases reduced temperature equals 8950 liters. The relative value<sup>2</sup> of blasting gelatine to nitroglycerol is as 1.4 to 1.45, Kieselguhr dynamite being taken as 1.0. Experiments made in lead cylinders gave the relative value of

Dynamite .....	1.0
Blasting gelatine .....	1.4
Nitroglycerol .....	1.4

LABORATORY,  
20 CULLUM ST., E. C., LONDON,  
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## NOTES ON LÖWENTHAL'S METHOD FOR THE DETERMINATION OF TANNIN.

BY HARRY SNYDER.

Received September 29, 1893.

THE determination of tannin is a difficult chemical problem, and to meet this difficulty no less than sixty methods and modifications have been proposed. As early as 1870, Dr. Günther, in the *Chemical News*, said that "none of the different methods for the determination of tannin answer the purpose equally well; that is, a method that yields excellent results for the tannin in nut-galls is not applicable to the tannin in sumac."

<sup>1</sup> Explosives and Their Power, M. Berthelot.

<sup>2</sup> Messrs. Roux and Sarrau.

Nearly all of these various tannin methods in principle follow one of four or five main lines: (1) The tannin is precipitated and determined as metallic tannates; (2) it is precipitated with hide powder and the tannin determined indirectly from the difference between the density of the solution before and after the precipitation; (3) it is determined colorimetrically or (4) by oxidation methods such as the Löwenthal.

The Löwenthal method is generally considered the most reliable, and is unquestionably the best method for commercial purposes. No attempt is made in these notes to compare the various tannin methods and discuss their merits or demerits, but simply to record some of the difficulties that are usually experienced in becoming acquainted with the Löwenthal method. Full directions and all of the details of the method are given in the last editions of both Sutton and Allen, but the various pitfalls in the workings of the method are not sufficiently noted.

In order to facilitate matters a brief outline of the method is given. The solutions and reagents employed are: (1) A standard solution of potassium permanganate; (2) a standard solution of indigo sulphate; (3) dilute sulphuric acid 1 : 4; (4) a solution of gelatine, twenty-five grams per liter.

The permanganate oxidizes the indigo, tannin, and all other organic matters that are present and are oxidized under the conditions of the titration. Let this amount of permanganate be denoted by  $a$ . The indigo is employed as an indicator, and is titrated against the permanganate either before or after each determination, and the solution is usually of such a strength that ten cc. is equivalent to five cc. of the permanganate; let this factor be denoted by  $b$ . The tannin is removed by precipitation with gelatine, and the soluble non-tannin organic matters oxidized by the permanganate; let this amount be denoted by  $c$ ; then  $(a-b) - (c-b) = x$ ,—the amount of permanganate necessary to oxidize the tannin, from which the equivalent amount of tannic acid is determined. The value of  $x$ , it will be seen, depends upon the accuracy of at least three permanganate titrations upon an unknown number of organic compounds, all capable of reacting differently with the permanganate under different conditions.

The main points to be observed are: (1) The care and prepar-



tion of the gelatine solution ; (2) the titration of the non-tannin materials ; (3) and the end point of the reaction.

The gelatine solution should be sterilized otherwise the solution frequently becomesropy and liquid in a short time, on account of the action of micro-organisms. Blank determinations should be made with the gelatine, and corrections made for all oxidizable materials that it may contain and give up to the filtrate. Frequently the results are too low on account of too large a factor being deducted for the non-tannin materials, when a small portion is due to the gelatine. Qualitative tests should also be made to determine whether or not the tannin has been completely precipitated. A hot filtration funnel can be employed to advantage, and the gelatinous precipitate washed by decantation until no qualitative test can be obtained for tannin.

The oxidation of the non-tannin materials is one of the chief causes of trouble, and since these compounds are present in both initial and subsequent titrations, great care should be taken to have all of the conditions the same throughout the entire process. As in the oxidation of organic matter by permanganate in water analysis, the degree of oxidation is proportional to the length of time allowed for the action of the permanganate, as well as to the temperature employed for the reactions. Should the first titration be carried on at a higher temperature or require a longer period than the second titration, the factor for the non-tannin materials would be a variable, and the results would be that the tannin factor would also be a variable. This source of error can be brought under control by strict uniformity in each operation.

The end reaction is quite marked, and after some acquaintance with the titration it can be predicted from the intermediate changes of color. The color of the solution at first is dark blue. The permanganate can be run in, drop by drop, until the color changes to a faint blue tint ; the cautious addition of only a few drops more will produce the desired yellow tinged solution with a pink shaded ring around the edge of the porcelain dish. Should this point be passed, one or two cc. of the indigo solution can be added, and the titration completed. In the calculation of the results make the necessary corrections for all indigo so used.

It is advisable at the outset to become acquainted with the workings of the method, using a good commercial sample of tannic acid, before attempting to determine the tannin in oak bark, tea, or other tannin yielding materials.

UNIVERSITY OF MINNESOTA,  
LABORATORY OF THE  
COLLEGE OF AGRICULTURE.

## THE CHEMICAL INDUSTRY OF THE UNITED STATES.<sup>1</sup>

BY HENRY BOWER.

THE chemical industry of the United States, in common with the other leading branches of manufactures, shows a remarkable increase in the decade between 1880 and 1890, and this is accompanied, in some instances, by results of such magnitude as to become phenomenal.

### TOTALS OF PRODUCTIONS OF CHEMICALS IN THE UNITED STATES IN 1890.

	Value.
Alum (94,174,008 lbs.) .....	\$1,625,210
Coal tar products .....	687,591
Dyeing and tanning extracts and sumac .....	7,947,841
Gunpowder and explosives (108,735,980 lbs.) ....	10,802,131
Fertilizers (1,818,552 tons) .....	34,038,452
Paints, white and red lead colors, and varnishes	52,434,690
Pharmaceutical preparations .....	16,486,643
Potash and pearlash (4,874,439 lbs.) .....	185,247
Sodas (329,369,633 lbs.) .....	5,384,400
Sulphuric acid .....	6,522,591
Wood alcohol and acetate of lime .....	1,885,469
Chemicals, including all acids, bases, and salts not heretofore enumerated .....	25,140,425
All other products .....	12,903,943

\$176,044,633

*Sulphuric Acid.*—The most important of all chemical manufactures is sulphuric acid, which maintains its supremacy over any other known article in promoting the manufacturing interests of the world. The large increase in the number of establishments and in the quantity produced indicates the advance that has been made in general manufactures in the United States during the last decade.

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893.

During the year ending June 30, 1890, the following quantities of sulphuric acid were manufactured:

50° B.,	948,129,821 lbs.,	valued at	\$3,299,707
60° B.,	19,078,597 "	" "	112,540
66° B.,	328,101,657 "	" "	3,110,344

Total value, \$6,522,591

This includes the 50° acid used in the manufacture of fertilizers.

In order to obtain an intelligent comprehension of the extent of the entire sulphuric acid industry, it is advisable to reduce the foregoing figures to one uniform basis, that of 66° Beaumé acid (oil of vitriol). As this contains from ninety-three per cent. to ninety-four per cent. of real monohydrate acid ( $\text{H}_2\text{SO}_4$ ), the reduction is made by multiplying the pounds of 50° acid by  $\frac{100}{93}$ , and the pounds of 60° acid by  $\frac{100}{94}$ . By so doing we obtain the following results:

Strength, Degrees Beaumé.	Pounds of acid as manufactured.*	Equivalent to pounds of 66° acid.	Value.
50 .....	948,129,821	632,086,547	\$3,299,707
60 .....	19,078,597	15,898,831	112,540
66 .....	328,101,657	328,101,657	3,110,344
		976,087,035	\$6,522,591

The total quantity of sulphuric acid produced in the United States reduced to a uniform strength of 66° B. is accordingly 976,087,035 pounds, or 488,043 tons of 2,000 pounds each.

Reducing the quantity produced to a uniform strength of 50° B., we have results as follows:

Strength, degrees Beaumé.	Pounds of acid as manu- factured.		Equivalent to pounds of 50° acid.
50 .....	948,129,821	× 1.00	948,129,821
60 .....	19,078,597	× 1.20	22,894,316
66 .....	328,101,657	× 1.50	492,152,485

Total 50° acid manufactured, 1,463,176,622, equal to 731,588 tons.

Supposing all the acid chambers to be running 365 days to the year, we find the amount manufactured in twenty-four hours to be 4,008,703 pounds, or 2,004 tons.

*Fertilizers.*—From a technical point of view, manufactured

manures become the next in importance to sulphuric acid in the category of chemical productions. The total of 1,818,552 tons of these materials produced during the year ending June 30, 1890, indicates by no inaccurate analogy the extent of the farming interests of the country. When we consider that about 300 pounds of artificial fertilizer are commonly used to the acre, it is seen that 12,123,680 acres were enriched by its use.

The increase in manufacture and consumption over 1880 is 1,091,099 tons, or about 150 per cent. These figures show with distinctness that large areas of our country are becoming unprofitable to farm without the use of these aids to fertilization. The existence of factories in the states of California, Illinois, Indiana, Michigan, Minnesota, and Wisconsin, is indicative of the gradual exhaustion of soil that was virgin in character less than twenty years ago. These facts tend to show that the time is approaching with rapid pace when none of our unmanured soils will yield in remunerative quantity. They prove also that economies are gradually being practiced in the utilization of material that formerly ran to waste.

In this respect the farmer occupies a reversed position to that of the manufacturer of artificial manures. By prodigal wastefulness and culpable ignorance he permits immense quantities of manurial matter to find its way to the sea, while bemoaning his lot and sighing over the yield of virgin lands in comparison with that of his own; whereas the manufacturer, by the aid of chemical skill and mechanical devices, converts refuse matter into valuable merchandise.

The advance in this branch of manufacture should give encouragement to the farmers of the Atlantic slope. When the no distant time arrives for the extinguishment of an agriculture that is based on primordial soil, the lands of these regions will recover their lost value, for observation will show how closely fertility is allied to the production of these manufactured manures, which can be carried on most profitably at those points where supplies of foreign crude material are obtained and where sea-board transportation can be made available.

*Soda.*—The last decade is rendered memorable to the chemical industry by the permanent establishment of the manufacture

of soda salts in the United States. Hitherto all attempts to produce these articles successfully from common salt have failed. The causes that have led to repeated failure and the consequent loss of large sums of money are to be found in the high cost of labor, the absence of customs duties on bleaching powders, or chloride of lime, and the exceedingly low rates of freight that rule on this class of merchandise.

The Solvay Process Company, of Syracuse, New York, has been founded on the experience and skill of the noted Solvay of Belgium. But, however satisfactory the process may be, it has a defect that enters into the production of many articles in the United States, notably in bleaching, paper-making, and chemical works, inasmuch as all the chlorine of the common salt employed is lost, passing away as valueless chloride of calcium. Consequently the United States still remains dependent upon Great Britain for its supply of so important an article as bleaching powder. A question of the greatest interest centers in this problem, how to overcome this defect in our manufacturing system. The efforts of inventors have for many years been directed toward the solution. Theory has marked out a number of paths, but practice has not yet succeeded in following any of these to a satisfactory result.

It may be added that, in addition to bleaching powders, the important chemicals, alizarin, chlorate of potash, and chlorate of soda, are not found among the salts produced in this country; and that these articles, so essential to the textile interests, are free of customs duty.

*Pharmaceutical Preparations.*—The United States is preeminent in the manufacture of pharmaceutical preparations, which are produced in consequence of the demand by physicians for more palatable or more compatible material for the *materia medica*. These articles cover a large field; they include pills, lozenges, fluid extracts, and a great variety of elixirs. The title, "elegant pharmacy," conveys a correct idea of the position occupied by the industry. Medicinal substances are associated in the mind with *ad nauseam* doses. The producers of pharmaceutical preparations have succeeded, in most instances, in masking or altogether obliterating the unpleasant properties

of drugs, which marks an advancement of no small moment within the past twenty years, inasmuch as this tends to improved health, greater security from disease, and a consequent reduction of the death rate.

The cost of distilled spirits constitutes the largest outlay in the manufacture of pharmaceutical preparations. A special investigation made by the census office of the United States showed that during the year ending December 31, 1889, 10,976,842 proof gallons of distilled spirits were consumed in the arts, manufactures, and medicine.

*Chemicals and Dye-stuffs Used in the Industry of Dyeing and Finishing Textiles.*—In 1890 the value of chemicals used in independent dye works, bleacheries, and print works was \$8,407,693. Much of the dyeing and finishing, however, is done by the manufacturers of the fabrics themselves, and the value of the chemicals and dye-stuffs is to be added to the amount named.

There were used by these manufacturers during 1890 the following amounts of chemicals and dye-stuffs:

Woolen mills.....	\$6,453,665
Cotton " .....	4,266,773
Silk " .....	558,532
	<hr/>
	\$11,278,970

Adding this \$11,278,970 to the value of the articles used by the dye works, bleacheries, and print works (\$8,407,693), we obtain as the grand total of chemicals and dye-stuffs used in manufacturing, dyeing, and finishing textiles, the value of \$19,686,663,—nearly twenty millions of dollars.

*Compressed Ammonia Gas, or Anhydrous Ammonia.*—The use of this article has reached large proportions within the past few years, and it has proved an invaluable aid to the preservation of food, the refrigeration of malt liquors, and the manufacture of ice. The introduction of the use of anhydrous ammonia has given great impetus to the manufacture of the special machinery adapted to its employment in the departments named.

The United States can rightfully claim the inauguration

on a large scale of these processes, which at this time yield profit, convenience, and health to people throughout the world.

*Fuel.*—Together with the metallurgical operations of smelting, melting, and heating, the chemical industry is a large consumer of fuel, hence great interest attaches to its supply; it is a figure of great importance in computing the costs of these manufactures.

Many fuel-saving devices are to be found in chemical works, and within the past two or three years fuel oil has become of considerable importance. Numerous devices have aided in making it adaptable in an admirable manner to furnace works. The replacement of coal is likely to be quite marked if the relative prices of the two fuels shall remain at the present ratio.

Natural gas also has been utilized in chemical works in localities adjacent to a supply, and its use has proved a great convenience.

*Labor and Wages.*—The employees of chemical manufacturers range from the lowest order to the highest in the scale, and the wages paid vary in proportion. Many operations partake of the "double shift," or twelve hours, the work being continuous, hence the average paid per hand reaches the high figure of \$580 per year. Eleven dollars and sixty cents per week is the average pay, counting fifty weeks steady employment in the year. A few females and a small number of boys find occupation in this department of manufacture. The men are chiefly of the able-bodied class.

The chemical, in comparison with such great industries as iron and steel, woolen and cotton, takes rank as the fourth among these great manufacturing divisions of the country. It represents a diversity of interests such as center in no other department, and it affords to the United States a source of activity for labor, skill, and capital, that is highly encouraging to those who have pride in the progress of their country.

The chemical industry of the whole world is interested in and relies upon certain tables or ready reference calculations. These aggregations of figures are confusing to a certain extent,

owing to the variation of the bases of calculation. In chemical works in the United States tables will be found in use:

For weights.	For measures.	For specific gravity.	For temperature.
Avoirdupois,	English gallons,	Beaumé scale,	Fahrenheit scale,
Apothecary,	Wine " "	Twaddle " "	Celsius " "
Troy,	Metric, as liters.		Reaumur " "
Metric, as kilo-grams.			Centigrade " "

Growing out of these different guides we have endless difficulties unless the writer on a given subject succinctly states by which of the various standards he is governed.

The scale of Beaumé is rendered confusing at times owing to the difference of the modulus that is accepted.

The transmutation of one thermometric scale into another is daily necessary, while errors are frequently made by the difference in the gallon capacity in cubic inches.

The present is opportune for the discussion of this subject with the view of arriving at some deliberate attempt to produce conformity out of this bedlam of figures. The tower of Babel with its traditional confusion of tongues may be taken as representing the difficulties arising in chemical work and transactions. A committee consisting of representatives from each nation could be appointed whose duty it should be to formulate an international system of figures and tables.

Uniform methods and statements for these basal calculations would inure to the ease of commercial transactions throughout the world.

#### NOTE ON THE MANUFACTURE OF THE PRUSSIATES.

BY WALTER D. FIELD.

Received October 14, 1893.

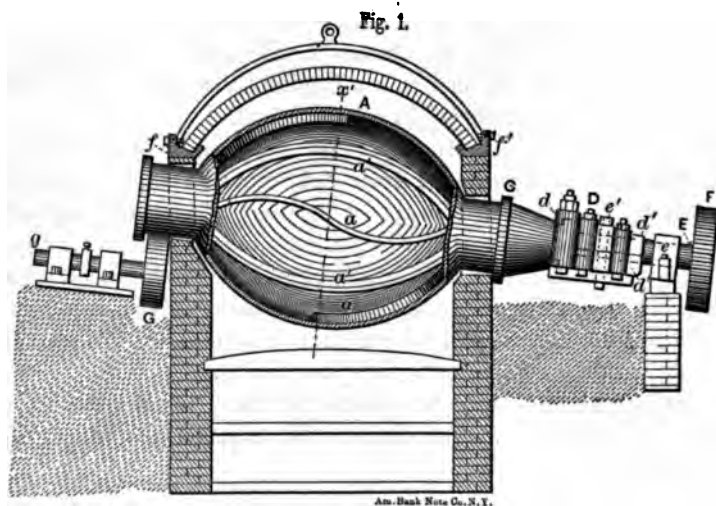
**I**N many branches technical literature is very incomplete. Descriptions of apparatus for the purpose of carrying on technical operations are reproduced in publication after publication. Authors are seemingly forgetful of the fact that the patents of this country represent in a large measure the progress of the various chemical industries.

In the "Fabrikation chemischer Producte aus thierische



Abfällen," by Hugo Fleck on pages 96 and 99 the same cut is given twice, and as if this were not quite enough to satisfy any one, the same cuts are reproduced in the fifth edition of Graham-Otto. Again in Thorpe's "Dictionary of Applied Chemistry" they are repeated. Before Graham-Otto was issued, Henry Bower received a patent (U. S. P., No. 210,086) for an apparatus that was an improvement on the old forms given in the German technical literature. His invention should have received at least a mention.

In the manufacture of potassium ferrocyanide, the iron is mostly obtained at the expense of the material of the melting

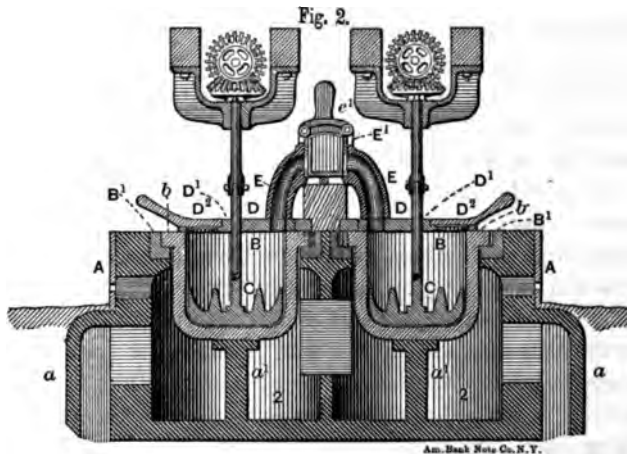


pot. A glance at the cuts given by Hugo Fleck will at once show the great loss of material and the expense involved in the renewal of the melting pots, the tearing down of the masonry, the resetting of the new pot, etc., etc. The life of the pots is very short at the best, and hence it is very desirable that they be used as long as possible without renewal and that they be easily set and unset.

In the apparatus represented by Hugo Fleck in Figures 29 and 30 there would be an abnormal waste of iron. The melt would consume the iron in the lower part, the part with which

it came in contact, and the remainder of the pot would be a complete loss. If the casting directly over the fire were increased in thickness so as to compensate for the loss of the iron in the melt, the retort would be heated unevenly and a proper condition of the melt could not be maintained.

Bower's apparatus was an improvement on the old forms in many ways, but still he did not reach the best possible results. In 1885 Carhuff received his patent, (No. 310,376,) in which his revolving furnace provides for the greatest consumption of the iron in the retort, and also makes it possible to maintain an equal temperature on all parts of the melt. The retort is easily



removed from the masonry and easily replaced. These retorts will last six weeks when in continuous operation. They are cast with the iron about one and one-fourth inch thick. Carhuff's revolving furnace marked an advance in the manufacture of ferrocyanide of potash and is the best method in use at the present time.

Figure 1 shows Carhuff's revolving furnace in part section and elevation, and Figure 2 shows Bower's melting pots in cross section.

## CARBON DIOXIDE AS A MEASURE OF THE EFFICIENCY OF VENTILATION.<sup>1</sup>

BY ELLEN H. RICHARDS, INSTRUCTOR IN SANITARY CHEMISTRY, MASSACHUSETTS IN-  
STITUTION OF TECHNOLOGY, BOSTON, MASS.

FROM the time of Hippocrates who gave as the sanitary maxim "pure air, pure water and pure soil," air has been placed first among the requirements of good sanitation. It is nevertheless a lamentable fact that, as Mr. Woodbridge has well expressed it, "the city which spends millions in water works for pure water supply and for sewerage for foul water removal, is still found tightening its purse strings when a few thousands are asked for to provide for pure air supply to, and foul air discharge from its school rooms."

The reason of this apathy is not far to seek. Chemists and sanitarians have seriously disagreed among themselves as to what constituted "bad air."

People live and apparently thrive among the most nauseous odors, while under more favorable conditions they sicken and die. One theorist has given a reason only to be forced to the wall by another quite as plausible. Between them the advocate of pure air finds slight hearing. It is only within recent years that a knowledge of the significant fact that not to air itself nor even to the bad odors it carries, but to the dust particles bearing living germs and spores is to be attributed the spread of disease, therefore filtered air like filtered water has become a necessity where dust cannot be avoided by scrupulous care.

And now with our increased knowledge of the causes which lead to liability to disease it seems probable that the chemist and sanitarian may at last unite in a winning fight for pure air. In a word, the new standpoint relates to the *resistance* which healthy blood and tissue present to the attacks of disease. This resistance is, we believe, due to the perfect nutrition of the blood corpuscles and this is largely dependent on the inhalation of air containing sufficient oxygen.

In vitiated air the blood becomes quickly loaded with imperfectly oxidized products which cause derangement more or less serious and finally render the individual, who is poisoned from

<sup>1</sup> Abstract of a paper read before the World's Congress of Chemists, August 26, 1893.

*within rather than from without*, more liable to succumb to disease.

If this view is in any measure correct it is important that chemists combine to urge upon the community the importance of a sufficient supply of air, especially in school rooms, and it is to be hoped that these views will command more respect than heretofore. It is notorious that even college halls and fine public buildings which should be examples, are in fact the worst of any buildings.

The Laboratory of Sanitary Chemistry at the Massachusetts Institute of Technology has had, for the past nine years, exceptional opportunities for the study of the relation of the amount of carbon dioxide to the efficiency of the ventilation, in that the Walker building is supplied with mechanical ventilation under the direction of an expert and in full control of the engineer who has records for all these years of the amount and temperature of air supplied to each room, and of the temperature of these rooms taken four times each day.

During these nine years some 5000 determinations of the amount of carbon dioxide have been made in these rooms by some 200 students.

Many problems have been studied and several reports published; without burdening this paper with details, to state a few of the conclusions reached may stimulate others to add to our too meagre knowledge on this subject.<sup>1</sup>

The outside air of the space around the Massachusetts Institute of Technology, Boston, varies from 3.7 to 4.2 parts carbon dioxide per 10,000.

The deterioration of the air as shown in the empty rooms is

<sup>1</sup> Papers relating to the points discussed, contributed in whole or in part from the Laboratory of Sanitary Chemistry:

"On the Determination of Organic Matter in Air." Thesis, by Marion Talbot, *Technology Quarterly*, 1, 1887-8.

"The Number and Distribution of Micro-organisms in the Air of the Boston City Hospital with some Carbon Dioxide Determinations." By Greenleaf N. Tucker in the twentieth annual report of the State Board of Health, of Massachusetts.

"A Critical Study of the Heating and Ventilation of the Walker building, Massachusetts Institute of Technology." By S. H. Woodbridge. *Technology Quarterly*, 2, p. 76 and 192, 1888-9.

"The Determination of Carbon Dioxide in the Air of Buildings." By A. H. Gill, *Journal of Analytical and Applied Chemistry*, 6, 1892. This paper gives the method in detail which is used in the laboratory.

about 0.5 part, due to the decomposition of the organic matter present in the flues, the floors and in the walls.

The air of the building in general, halls and drawing rooms, reading rooms, etc., which are open and in which people are constantly moving, is maintained at about 5.0 parts as an average of examinations during eight years. In the ninth year there has been an increase due to an increased number of lecture rooms on the second floor.

The air of most of the lecture rooms has contained from six to eight parts; of the larger crowded halls for 200 or more students, ten to twelve parts according to weather, whether it is clear and dry and with a strong wind, or whether the air is loaded with moisture and is still.

From this experience it would seem that students can work well in a clean room with about seven parts per 10,000 of carbon dioxide; much more than this causes dullness, and anything over thirteen parts causes in most cases an almost impassable barrier to the full acquisition of knowledge.

When churches, halls, and lecture rooms usually show from fourteen to eighteen parts per 10,000 in twenty minutes after the audience assembles, it is not strange that eloquence often fails to arouse enthusiasm.

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## AN INTERNATIONAL INDEX TO CHEMICAL LITERATURE.<sup>1</sup>

BY H. CARRINGTON BOLTON.

DURING one of my bibliographical tours in Europe, an eminent librarian of a German University remarked: "You Americans are doing more and better work in bibliography than all the nations of Europe taken together." And this he said not in flattery but as the expression of an earnest conviction. Later I expressed surprise that Germans with such splendid collections of books and other advantages should leave it to Americans to cross the Atlantic and wrest from Europe materials for general and special bibliographies. To this he promptly replied: "Ach mein Freund, das Geld fehlt!"

I shall not attempt to demonstrate the accuracy of the gentleman's statements, as it would involve comparisons, and these

<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

are said to be odious. A basis for his enthusiasm is, however, found in such monumental works as Pool's Index, Fletcher's Index, Billing's Index-catalogue of the Medical Library of the Surgeon General's office, the Index-Medicus edited by Dr. Robert Fletcher, the catalogue of the Boston Athenæum, as well as the bibliographies of science published by the Smithsonian Institution, by the U. S. Department of Agriculture and in independent journals. Many other notable works will suggest themselves to the chemists present who will understand that this is only a passing reference.

The production of special and general bibliographies in the United States goes forward with the multiplication of public and endowed libraries, now increasing in number and value with gratifying rapidity throughout the land. Some of these are publishing bibliographies of specific subjects in addition to their Library Catalogues; in this direction Harvard University takes the lead. Unfortunately much good work done by institutions does not get beyond the MS. stage, as for example the Subject-Index in preparation at the Scientific Library of the U. S. Patent Office; and the chemical bibliographies compiled by the students of the University of Michigan as appendages to theses in science.

There are at least three organizations in the United States which promote the preparation of bibliographies; these are (1) the American Library Association, (2) the Committee on the Bibliography of Geology appointed at the International Congress of Geologists, and (3) the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science. The work of the American Library Association is familiar to everyone; through the journal it reaches all librarians and bibliographers in sympathy with its enterprises. Its scope is, however, almost entirely literary and science finds little place in its admirable plans.

The secretary of the Committee on the Bibliography of Geology appointed at the International Congress of Geologists held September 1, 1891, at Washington, has issued a circular dated November 20, 1891 which sets forth its plans for work. These comprise the preparation of (1) a list of the geologic bibliogra-

phies already in existence, (2) new bibliographies of special topics, and (3) the periodic registration of the current bibliography of geology.

Their work has been so recently begun that as yet great results can hardly be expected.

The work of the Committee on Indexing Chemical Literature, of the American Association for the Advancement of Science, now in the eleventh year of its existence, is familiar to most persons present. This committee has endeavored to direct attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little systematic work has been undertaken, duplication of labor has been prevented and independent efforts have accomplished much. Thus a collection of special bibliographies has been gradually forming, which now number more than fifty; the list was printed in the tenth annual report of the committee published in the proceedings of the A. A. A. S. for 1892. While the committee feels that their labors have not been in vain, the proportion of the completed bibliographies to the number of authors publishing chemical papers is still unhappily small, and the average of five bibliographies per annum is rather lower than expected. The committee expresses the hope that the number will grow much faster in the future.

In England the British Association for the Advancement of Science has done something towards fostering the object under consideration, by appointing committees on Indexing Solutions and other topics, but their work progresses slowly.

The chemical societies of Berlin, Paris, and London, give to their members and subscribers, laboriously prepared abstracts of papers published in countries other than their own. For persons whose linguistic attainments are limited to their mother-tongue these abstracts are undoubtedly useful, perhaps invaluable; but it rarely happens that they can be entirely relied upon for the details needed by chemists practically interested, and the originals must eventually be consulted. It has seemed to me that if the same amount of energy expended by abstractors of the societies named could be exerted in indexing, greater practical results would be obtained, and at far greater economy of space.

Moreover these societies generally confine their abstracts to publications issued in other countries than their own, and consequently a large amount of good material published at home in Government reports, transactions of learned societies, and periodicals devoted to general science, escapes the eyes of all except a few industrious readers.

It has further occurred to me that the chemical societies of Germany, France, Italy, England, Russia, and the United States, instead of filling their official organs with abstracts of papers foreign to each, might well devote their energy to indexing the wealth of material produced each in its own nation. And this brings me to the statement of a plan which I have the honor to propose to this Congress, for a Co-operative International Index to Chemical Literature.

I suggest that this Congress, in which are representatives of the six leading chemical societies of the world, recommend to these societies the preparation of an annual index to current chemical literature, each society to care for the productions of the country in which it is situated. These annual indexes to chemical literature could be published in the journals (*Berichte*, *Bulletin*, *Journal*, etc.) of the respective societies, which fortunately for our purpose are all in octavo form, and when all the indexes are issued for a given year, they could be bound together for convenience. The bibliographies would of course be compiled, on the same or similar plans, this uniformity being secured by conference between the Index-Committees of the several societies. This plan would necessitate the consultation of six alphabets at least in each annual volume, but this inconvenience would be counterbalanced by the greater accuracy and fullness attained by the subdivision of labor here proposed.

What reception this plan may receive by the several societies is uncertain, but I believe that no more important work can be undertaken by the American Chemical Society. This newly re-organized association now numbers over 700 members and is a truly national society; the "Journal" could not present to its members and subscribers a more welcome contribution than a subject-index to the publication of American chemists. This might be done half yearly, or better quarterly, and should embrace the



widest range of pure and applied chemistry. Perhaps the American Chemical Society will lead in this enterprise, and then the older and more conservative societies of Europe might follow. One stimulus that would eventually influence them is national pride.

So far, this plan relates to current literature and some provision must be made for indexing the enormous accumulation of material already in print.

Probably there is no better way to attack this problem than to prepare a subject-index to the chemistry contained in the Catalogue of Scientific Papers published under the auspices of the Royal Society. This monumental work loses much of its value owing to the lack of a subject-index, and it is deeply to be regretted that there is no prospect of one being compiled, if at least one may judge from the correspondence on this subject printed in the pages of *Nature*.

And here allow me to place on record a fact bearing on the question; a few years ago a member of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, already known to the scientific world by his labors in bibliography, decided to undertake the preparation of a subject-index to the chemistry and physics in the eight quarto volumes of the work named, but before doing so wrote a courteous letter to the secretary of the Royal Society announcing his scheme. In that letter the gentleman explained that he planned to compile the subject-index and to print it entirely without expense or liability on the part of the Royal Society.

After a long lapse of time the gentleman received a note from the secretary of the Royal Society stating that the matter had been laid before the council and they had refused permission to have such an index prepared! Thus rebuffed my friend abandoned his scheme and turned his attention to another task.

In spite of this attitude of the council of the Royal Society, I believe a regularly constituted committee of chemists could secure permission, if indeed necessary.

Details of methods to be pursued cannot here be considered; they could be formulated by a committee.

A general bibliography of chemistry has been recently at-

tempted by the writer of this communication; the results form a volume of over 1,200 pages just issued by the Smithsonian Institution as one of the series entitled Miscellaneous Collections. This "Select Bibliography of Chemistry, 1492—1892" embraces about 12,000 titles in twenty-four languages, yet makes no claim to completeness; it is moreover a bibliography, not an index.

In conclusion I have the honor to propose the appointment of an International Committee on Chemical Bibliography, to consist of one member from each country represented in this Congress. That this committee have unlimited power to add to its number, provided however no country have more than two representatives. That this committee, through the European and American Chemical Societies, report a scheme for an International Co-operative Index to Chemical Literature.

UNIVERSITY CLUB,  
NEW YORK CITY,  
August, 1893.

[EDITORIAL NOTE.—A committee consisting of Edward Hart, R. B. Warder, and Wm. L. Dudley was appointed by the Congress to consider the recommendations of Dr. Bolton set forth in the above paper. Their report with additional action by the Congress will be found on p. 309 of the June number of the *Journal* for this year.]

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## ACCURACY IN THE ANALYSIS OF DAIRY PRODUCTS.<sup>1</sup>

BY H. DROOP RICHMOND, CHEMIST TO THE AYLESBURY DAIRY CO.

### PART I. MILK ANALYSIS.

IN the July number of the *Analyst* for 1889 I published a paper on "Fat Extraction from Milk Solids;" the object of that paper was to show how the differences between the two rival processes of fat-estimation could be explained and rectified; I succeeded eventually in obtaining identical results by the processes due to Adams, Soxhlet, and Storch. Since that paper appeared it has been shown by Waller, Liebermann, and others that the processes of fat-estimation, especially the Adams method, should be modified by rendering the use of ether as a solvent inadmissible. The Werner-Schmid process has also come into extensive use.

In considering the accuracy of any process we have three

<sup>1</sup> Read before the World's Congress of Chemists, August 22, 1893.

methods of obtaining evidence of exactitude; first a synthetical method, that of taking known quantities of the substance to be estimated, mixing it with the substances from which it is to be separated, and performing an estimation; if the substance is recovered in totality, and in a state of purity, it is a proof of the exactitude of the method; a second method consists in the comparison of the results obtained by the process with those obtained by a process distinct in principle, and in which the probable error lies in a different direction; this method does not give a proof of exactitude, but only brings the chance of exactitude to a high degree of probability. The third method is to examine the errors of the method in detail, and to prove that they can be neglected or that they do not exist; this method would be good could we be certain that all possible sources of error were known to us. The largely used method of obtaining concordant duplicate determinations must be absolutely rejected as a method of proving accuracy; it only proves accuracy in manipulation, and sheds no light on the real errors of the process.

To prove the accuracy of the estimation of fat, as we cannot employ the synthetical method, we must prove that first the whole of the fat is extracted, and second that nothing else is weighed as fat. It is hardly necessary to bring forward other proof that the fat is wholly extracted than the agreement between the Adams method, the Werner-Schmid method, and methods in which the milk is dried on some medium such as plaster of Paris, kieselguhr, or pumice, and this residue is ground fine, extracted, and reground and re-extracted until nothing more is extracted. Figures showing these agreements have been published so often that it is not necessary for me to take up space by giving such results here. It has been alleged that ether extracts other substances than fat (Waller, *J. Am. Chem. Soc.*, **13**, 52; Liebermann, *Ztschr. anal. Chem.*, **35**, 168). Their conclusions to my mind are not satisfactory, as my experience tends in a contrary direction. As an explanation of the results found by Waller and by Liebermann I may mention that the paper coils on which they experimented contain matter soluble in ether and totally removed with exceeding difficulty. These coils always give when extracted with ether a quantity

of loose fibers; and commercial ether contains many impurities, such as water and alcohol, and these impurities may cause the appearance of substances other than fat in the extract. I am in the habit of purifying my ether by washing with water, shaking with a large quantity of anhydrous calcium chloride and distilling. For special use the distilled ether is rendered anhydrous by keeping over sodium, and distilling portions as wanted. I have already published experiments showing that ether, petroleum ether, and chloroform give the same results, if the time of extraction is sufficient (*J. Anal. Chem.*, 4, 26, 241). I have further narrowed down the substances that can be extracted by ether from albuminoid by comparing the fat estimated by the Adams, the Werner-Schmid, or the Storch processes with that extracted from the casein or from the precipitate obtained in the Ritthausen process. As examples of the agreement the following figures may be quoted:

Fat from albuminoid.....	4.93	2.87	1.38	4.00	0.04
Fat, Adams, etc.....	4.97	2.89	1.43	3.99	0.17

In the last case (a separated milk) the casein was dissolved in ammonia and the solution placed on an extracted Adams coil, and a further amount of 0.12 per cent. of fat was obtained. As the hard horny mass of albuminoid is a most unsuitable medium for extraction I am of the opinion that the slight deficiency of fat extracted from albuminoid is due to incomplete extraction and not to the extraction of other substances from the total milk solids. It only remains to prove that no albuminoids are extracted by ether. The absence of nitrogen in the extract is I think sufficient proof of this. The next problems that confront us are, does the fat itself dissolve anything from the milk and if so should it be considered as a constituent of the fat, and does the weight of fat extracted represent the weight of fat in the milk or does it increase or decrease in weight during the extraction and drying, and if so can the amount of change be neglected as being too small to affect the results to any practical degree? My experiments (*loc. cit.*,) show that the acidity of the extract is practically the same whether ether, petroleum ether, or chloroform be used as a solvent, and therefore that if lactic acid be extracted it must be dissolved in the fat. The agree-

ment between the extraction from albuminoid and from milk solids shows the same thing, as the lactic acid if not in solution in the fat must have been washed away in the former case. I do not know of any other substance which exists in milk and is soluble in fat. I do not think on the whole that any correction need be made for anything soluble in the fat; but before an authoritative opinion can be given on this point an extended research must be made. Fat on drying at the temperature of boiling water undoubtedly increases in weight; but my experiments have shown that during the half hour or so during which the fat is dried the increase does not amount to more than 0.2 per cent. of the weight of the fat. Even if weighed quantities of fat are placed on some medium and extracted as in a milk analysis no appreciable deviation from the weight taken can be detected. I have concluded that the change in weight during extraction can be neglected, and that the weight of fat extracted can for practical purposes be taken to represent the weight of fat in the milk.

My general conclusions are:

1. That ether, petroleum ether, or chloroform are equally efficient solvents, if sufficient time be allowed for extraction, but that ether is the most convenient, as it extracts the fat more rapidly.
2. That an accurate estimation can be obtained only if the milk solids are subdivided either by the use of a paper coil free from matter soluble in the solvent, by evaporation of the milk on some medium which can be very finely divided, or by extraction from a solution in which every thing except the fat is dissolved (as in the Werner-Schmid process).
3. That if ether is used as a solvent it must be pure and anhydrous.
4. That the weight of fat obtained in the analysis may be taken to represent without appreciable error the amount originally existing in the milk.
5. That in order to minimize the chance of error due to impurities in the media used for extraction, change of weight of the vessels used to weigh the fat in, etc., it is advisable to do a blank experiment following the conditions of the actual experi-

ment as far as possible. I am in the habit of taring my flask against the flask in which the blank experiment is performed.

6. That it is necessary to secure a true average sample of the milk. The milk must be well mixed by slight agitation, and if a pipette is used it should have as wide an opening as possible to minimize the danger of separation of the cream during the passage through the narrow opening.

On the whole I am inclined to consider the fat-estimation one of the most reliable figures obtained in a milk analysis.

*Estimation of Total Solids and of Water.*—We may rule out all methods as inaccurate which fail to give a constant weight on continued drying, or which show signs of decomposition of the residue weighed, such as marked browning of the residue. For this reason Wanklyn's three hours method is inadmissible, though it has been claimed by him that it is the more accurate in that the water of hydration of milk sugar is not driven off during this period. Even were this the case, though no experimental proof has been attempted, it would be no argument for the greater exactitude. It would be equally reasonable to object to the determination of (say) sodium sulphate in a solution by evaporation, because the residue weighed does not represent the hydrates which occur in the solution. The method adopted by the Society of Public Analysts must also be rejected, as constancy of weight is not attained, and the residue shows marked browning. Of methods which I have found to comply with the conditions stated above I may mention that of taking about one gram of milk and evaporating in a large platinum basin with constant agitation of the basin while evaporating, to spread the milk over a large surface, and that of evaporation on some substance which largely subdivided the milk. Of these substances I give the preference to asbestos, on account of the fineness of the fibers, and the ease with which it can be reduced to constant weight which does not vary during the experiment. It must be borne in mind, however, that a very finely divided substance condenses more air on its surface than one which is of larger grain; and if accuracy is desired to the second decimal place or beyond all weighings must be made in vacuo. I mention this as milk analyses are frequently stated to the third deci-

mal place, and the analyst may be therefore presumed to have desired an accuracy to the second decimal place. I am not in favor of enclosing the substance on which the milk is placed in a vessel of glass, as this is more liable to change in weight than platinum, and the same remark applies with more force to any connections of cork or India-rubber that may be included in the weighed portions of the apparatus. I do not see a way of proving the accuracy of the estimation of total solids other than the combined evidence of the attainment of constant weight, absence of apparent decomposition, the comparatively near agreement of total solids estimated with that deduced from the fat and specific gravity by an appropriate formula, and the near agreement to 100 per cent. of complete analyses. The evidence afforded by the two latter methods of those I have selected as the most reliable methods, I propose to give here. The probable error of specific gravity determinations is in my experiments  $\pm 0.00006$ , which would produce a probable error in the fat calculated of  $\pm 0.015$  per cent. Three series of fat determinations gave :

	Per cent.	Experiments.
1. Adams method.....	$\pm 0.031$	67
2. Werner-Schmid method .....	$\pm 0.040$	19
3. Both methods compared.....	$\pm 0.036$	15

The total probable error of these three series is 0.035 per cent.

The probable error of total solid estimation is from the results of eighty-one experiments  $\pm 0.021$  per cent.

Assuming that the combined probable error of the three series is the square root of the sum of the squares of the three probable errors, this stands at  $\pm 0.043$  per cent. The probable error between estimated and calculated fat is  $\pm 0.067$  in 132 experiments (using the formula which is best suited to the results), and this gives a probable error of  $\pm 0.043$  per cent. of fat or of  $\pm 0.0002$  in the density for the variations due to differences of composition of the solids not fat, and for Recknagel's phenomenon; this certainly does not exceed my estimate of the error.

This method of calculating the accuracy of total solid estimation is only of service in showing that the method gives constant results, as we do not know the true formula for calculating the fat, it being deduced from the results themselves.

As evidence of accuracy shown by a near agreement to 100

per cent. in complete analyses, it may be stated that analyses add up to 99.8 per cent. when acidity, basic constituents, and salts other than the ash are not estimated; and the deficiency of 0.2 per cent. is, I conclude, a near approximation to the amount contained in milk. The estimations I have made give on an average about 0.05 per cent. of bases in milk and about 0.05 per cent. for the salts not included in the weight of the ash; and as the milks were fresh when analyzed 0.1 per cent. is a fair approximation to the amount of the lactic acid. In one or two more complete analyses the totals have been between 99.9 and 100. I append five specimen analyses:

Water .....	89.46	86.89	90.55	87.22	87.14
Fat .....	1.44	3.99	0.27	4.36	4.49
Sugar .....	4.76	5.48	4.74	4.18	4.17
Casein .....	3.21	2.07	3.45	2.76	2.82
Albumen .....		0.19		0.41	0.42
Albumoses .....		0.30			
Bases .....	0.05	0.16			
Lactic acid .....	0.17	0.20			
Ash .....	0.76	0.59	0.78	0.78	0.78
Total ....	99.85	99.87	99.79	99.71	99.82

This last method is not a very satisfactory one for proving the correctness of the total solid estimation, as it is dependent on the assumed correctness of all the other determinations, and especially on the exactitude of the deficiency. Reviewing the whole of the evidence, I am on the whole inclined to conclude that the method I have adopted (Babcock's) is not affected by any serious source of error. It may possibly give too high results for total solids and too low results for water, as I find that by evaporation in vacuo, I obtain slightly higher results than at 100° C. but I see no way of proving that this is not due to incomplete evaporation.

As the two determinations, total solids and fat, and by difference, solids not fat, are those which are chiefly relied upon for judging the purity of milk, a few remarks on the accuracy with which conclusions can be drawn, will not be out of place here. The most widely known limits for pure milk are those of the British Society of Public Analysts, *viz.*, 3 per cent. of fat and 8.5 per cent. of solids not fat. These were originally



intended to apply to British dairy cows which are almost exclusively shorthorns, and for this cow the limits are reasonable. For breeds such as the Channel Island cattle they would be too low, while, for instance, for Holstein cows they would be in many instances too high. Even taking shorthorns the limits are in rare cases overstepped. In the milk of single cows I have records of fat as low as 2.0 per cent. and solids not fat down to 7.7 per cent. in genuine samples. It would be manifestly unfair for a chemist to swear that every sample giving 2.0 percent. of fat or 7.7 per cent. of solids not fat was genuine, merely because one genuine sample out of many thousands examined gave such figures, and equally so to condemn every sample that was just below the limits adopted. With regard to low percentages of fat I see no way at present of discriminating between genuine milk low in fat, and milk from which part of the fat has been abstracted. I am not without hope that this may be accomplished. The size of globules, and the proportion of those of large to those of small size may afford a means to this end, and as cream undoubtedly contains a higher proportionate content of albuminoid, it is possible that an estimation of a deficiency of this in the milk may afford evidence of fat-abstraction. I have no evidence to offer on this point, but put forward the suggestions for the consideration of the Congress.

With regard to low solids not fat, much evidence can be obtained from a fuller examination. The whole of my experience goes to show that genuine milks low in solids not fat never furnish an ash of less than 0.7 per cent., while the majority of watered milks give an ash below that figure. Further the excess of ash in genuine milks is not due to chlorides or any water-soluble substance, but to insoluble phosphates. The ash of milk is neutral, is entirely soluble in dilute acids, and contains no boric nor carbonic acids. I have not found the nitrogen in genuine milks to fall below 0.5 per cent. A curious coincidence is that the percentages of nitrogen and insoluble ash are nearly the same in milk. I find an average of 0.531 per cent. of nitrogen and 0.530 of insoluble ash, with extreme differences of 0.02 per cent.

As many waters contain nitric acid, which I have never found in genuine milk, the diphenylamine test for nitrates is of service in deciding whether a given sample is adulterated. I curdle the milk by heating to near 100° C. and adding a small quantity of acetic acid, and filter the serum. I place a little diphenylamine in a porcelain basin and add one cc. of pure sulphuric acid, and allow a few drops of the serum to trickle down the sides of the basin over the surface of the acid. If nitric acid be present a blue coloration is developed in ten minutes round the edges. I have detected five per cent. of water in milk by this test.

If I find a milk of (say) eight per cent. of solids not fat, and I find in it nitric acid, and the ash falls below 0.7 per cent. and the nitrogen below 0.5 per cent., I condemn it; while if there is no evidence of nitric acid, and the ash is above 0.7 per cent., and the nitrogen above 0.5 per cent., and I find no extraneous body to account for the excess of ash and nitrogen, I decline to certify that it is watered, and should state that there was the strongest probability of its being genuine. I may cite examples:

Specific gravity ..	1.0280	1.0295	1.0290	1.0290	1.0285	1.0285	1.0290
Total solids .....	10.63	11.62	11.31	11.37	11.36	11.99	11.34
Fat .....	2.72	3.47	3.22	3.25	3.30	3.87	3.20
Ash .....	0.62	0.64	0.76	0.72	0.72	0.71	0.72
Solids not fat.....	7.91	8.15	8.09	8.12	8.06	8.12	8.14
Nitric acid .....	trace	trace	none	none	none	none	none
Conclusion .....	watered	watered	gen.	gen.	gen.	gen.	gen.

I did not determine the nitric acid in these samples, as other evidence was forthcoming to assist my conclusions.

The season of the year should also be considered. Thus in England the recent drought in June and July has caused the milk to be of poorer quality than has hitherto been recorded. It would be advisable in every country to establish a Government Laboratory to study the mensal fluctuations of the composition of milk, and to communicate the results to chemists charged with the working of the adulteration acts. In England no such laboratory exists but the function is very partially filled by a private dairy company of whose laboratory I have the honor to be in charge, and on numerous occasions I and my predecessor have been consulted by public analysts. The apparent

disadvantages of a trading company under the supervision of the adulteration act performing a function properly belonging to the state, only shows the necessity of the establishment of Government Dairy Laboratories. Other countries are more fortunate than England in this respect, and I have no doubt that representatives of those countries will testify to the usefulness of these laboratories.

*Estimation of Milk Sugar.*—Vieth's modification of Wiley's method of polarization (*Analyst*, 1888, 63) gives results which agree well with the gravimetric method of estimation by Fehling's solution. I am in the habit of making an estimation of the copper oxide reduced by a known weight of pure milk sugar, as nearly as possible equal to that in the quantity of milk taken for analysis, performing the two estimations under the same conditions.

The probable error of each estimation, and of the two estimations together was found to be  $\pm 0.06$  per cent. The work of Wiley on the polarization of milk sugar is so conclusive that it is not necessary to search for further proof of accuracy, but this determination may be accepted as one which can be depended upon.

*Estimation of Albuminoids.*—Chemists are far from being agreed upon the albuminoids existing in milk, thus the following chemists give as follows:

Bechamp .....	Caseinates, albuminates and galactozymase.
Biel.....	Syntonin.
Blyth .....	{ Casein, albumen, galactin, lactochrome (nuclein?).
Danilewsky ....	{ Caseo-protalbin and caseo-albumen (nuc- leo-protalbin and nucleo-albumen) and six other albuminoids.
Duclaux.....	Only casein.
Hammersten ...	Casein and albumen only.
Palm.....	Hemialbumose.
Sebelien.....	Globulin.

I have no hesitation in rejecting Duclaux's view that there is only one albuminoid, casein, in milk, as two certainly, having distinct properties and inconvertible, have been proved to exist in milk.

Hammersten and later Chittenden have disposed of Danilewsky's view, and with this the existence of lactoprotein, which is accepted by many, galactin, nuclein, and hemialbumose, becomes an untenable theory; as Blyth alleges the presence of only 0.01 per cent. of lactochrome in milk this body may be neglected. We are then reduced to casein, albumen, globulin, syntonin, and galactozymase. The first two are almost universally accepted; and as Halliburton now admits the correctness of Sebelien's observation that globulin exists in traces in milk, this may also be accepted: From an analytical point of view its presence can almost be neglected, as the amount present in normal milk is very small. The existence of syntonin and galactozymase cannot be considered as fully established.

I am inclined to favor Bechamp's view that casein and albumen exist in milk as salts, chiefly on account of the behavior of neutral milk with copper salts. I find that if milk be neutralized the albuminoids are completely precipitated by a solution of copper sulphate; and this would not be the case were there no base for the sulphuric acid of the copper sulphate to combine with. Soldner's work on the salts of milk (*Landw. Vers. Stat.*, 35, 351) offers some confirmation to this theory, as he finds in milk more base than will combine with all the acid that has been found. He attributes this excess of alkali to the fact that organic salts other than citrates occur in milk, but these have not yet been found (if we neglect Bechamp's acetic acid). Many of the reactions of the albuminoids in milk resemble those of casein or albumen dissolved in dilute alkali, for instance the behavior of heat on milk.

In the analysis of milk I regard the albuminoid precipitated by a saturated solution of magnesium sulphate as casein (including globulin), and the further precipitate by tannin or phosphotungstic acid in the filtrate from the casein as albumen (following Sebelien). If I have reason to suspect that from some change in the milk albumoses are present I separate the albumen by heating after slight acidification and precipitate by tannin. This precipitate I regard as albumoses; but the determination is not a very exact one. The precipitate produced by adding sulphate of copper to the neutral milk I regard as casein

and albumen and, following Ritthausen, designate this total proteids. A second determination of albumoses may be made in the filtrate from this; but the accuracy of this determination is questionable. I have only estimated albumoses in whey and mixtures of this with milk; and the two albumose determinations have been fairly concordant. I also calculate albuminoids from the total nitrogen, a method which may be expected to give results which are slightly too high.

I assume that both casein and albumen contain 15.7 per cent. of nitrogen. For albumen I believe that this is the correct figure, as both my own determinations and those of other observers are very close to that figure. For casein Hammersten gives 15.65 and Chittenden and Painter 15.91, so it is probable that no very great error is committed by taking it at 15.7 per cent.

In ten experiments the average difference between casein and albumen, nitrogen and total nitrogen is 0.02 per cent. with extremes of 0.00 and 0.05. The average difference between total proteids by copper sulphate method and total proteids by calculation from total nitrogen in five experiments is 0.17 per cent., with extremes of 0.10 and 0.27. In one experiment the casein and albumen together summed up to 0.21 per cent. less than the total proteids by copper; but in this case the total proteids by copper showed the minimum difference from the total from nitrogen and the casein and albumen nitrogen was 0.05 per cent. below the total nitrogen. The above figures show the error incidental to albuminoid estimations; but at the same time, though few in number, lead me to believe that the methods of albuminoid determination that I have adopted give fairly good results. A full description of the mode of working that I adopt is to be found in a paper by Mr. Boseley and myself in the *Analyst* for July of this year and need not be reproduced here. Bases I calculate in milk by multiplying the non-albuminoid nitrogen by 3.2; and this determination is of very questionable accuracy.

The estimation of ash calls for no remark. I may, however, remark that the ash does not represent the salts which exist in milk, as it contains phosphates obtained by the combustion of the casein, and does not include citrates which occur. These

two errors tend to compensate each other, though probably not entirely.

I do not propose to touch on the estimation of the small amounts of other bodies that have been described in milk, as I feel that our knowledge is not far enough advanced to permit of this, and in presenting this paper to the Congress I can only say that it is very incomplete and is to be considered more as a nucleus for discussion, and, I hope, concerted investigation than an exhaustive resumé of the subject.

In conclusion, I think that the methods that I have touched upon for the estimation of total solids and water, fat, ash, milk sugar, casein, albumen, and total proteids are not liable to any great error, and further that we are enabled to detect watering of milk with fair exactitude. The detection of fat abstraction is not so satisfactory.

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, Etc.*—504,665, September 5, Bradford, H., ore separating machine. 505,169,–505,412, September 19, McGlew, T., ore concentrator. 504,931, September 12, Monell, I. F., ore separator and concentrator. 504,923, September 12, Humphries, D. W., concentrator. 504,678, September 5, Fuller, W. M., amalgamator. 504,859, September 12, Boss, M. P., amalgamating pan. 504,508, September 5, Wiswell, J. C., amalgamating machine. 504,689, September 5, Albrecht, H. S., disintegrator for ores, etc. 504,548, September 5, Bauer, T., and Mendheim, G., coke-oven. 505,112, September 19, Ludwig, O., smelting furnace. 505,538, September 26, Sheedy, D., and Iles, M. W., blast furnace. 505,549, September 26, Iles, M. W., tuyere. 505,551, 505,552, September 26, Iles, M. W., process of and apparatus for treating slag. 504,666, September 5, Bradford H., process of concentrating ores by gravity, on a shallow basin over which water flows, the table being jarred to facilitate separation.

*Gold and Silver.*—504,706, September 12, Calhoun, H., extraction of metal from ores; roasting in presence of carbon and ammonium chloride.

*Iron and Steel.*—505,132, September 19, Sague, S. A., manufacture of sheet iron or steel, apparatus for. 505,131, September 19, Sague, S. A., galvanizing sheet metal. 504,322, September 5, Brustlein, H. A., mold for casting ingots. 505,728, September 26, Shaw, A. J., soaking pit for ingots.

*Zinc.*—505,408, September 19, Moore, G. E., willemite and franklinite, in limestone gangue, are calcined in non-reducing atmosphere, the lime

is allowed to slake, the zinc ore is separated from manganese and iron ore, which latter is smelted in the blast furnace for spiegel, while zinc is extracted from the zinc ore.

*Aluminum*.—504,324, 504,325, September 5, Case, W. E., manufacture of aluminum fluo-sulphate free from iron.

*Ammonia*.—505,427, September 19, Vail, G. L., and Charlton, T., purification of ammonia gas; by passing gas under pressure of 9-12 atmospheres through saturated aqua ammonia, at a temperature low enough to condense moisture and impurities.

*Brewing, Etc.*—504,478, September 5, Meyer, G. J., malting apparatus. 505,239, 505,240, September 19, Theurer, J. F., apparatus for charging liquids with carbon dioxide.

*Water*.—505,641, September 26, Rochlitz, W., water distilling apparatus.

*Alkaline Phosphate*.—504,453, September 5, Meyer, T., sulphate of an alkali is treated with phosphoric acid in presence of limestone at a low temperature.

*Sewage Purification*.—505,182, September 19, Adeney, W. E., and Parry, W., after separating the solid matter, sodium manganate is added and the manganese is recovered and converted into manganate again.

*Organic Compounds*.—505,113, September 19, Majert, W., and Schmid, A., piperazin hydrate; having formula  $C_{14}H_{10}N_2 + (1+6)H_2O$ , a strong solvent of uric acid and without caustic properties. 504,905, September 12, Borgmeyer, C. L., pyroxylin solvent and its compound; the solvent named is artificial oil of peppermint in amyl alcohol, and the compound is pyroxylin dissolved in artificial oils of tansy, peppermint, red thyme, and sassafras. 505,755, September 26, Drewson, V. B., recovery of organic substances from sulphite liquors; by treating with milk of lime at 100° Celsius and under pressure. 505,395, September 19, Engle, J. P., apparatus for treating waste products of petroleum. 505,416, September 19, Bell, A. F. L., process of extracting and refining asphaltum. 504,626, September 5, Schmid, J., medicinal compound;  $C_6H_4 \cdot \frac{N=CC_6H_4OH}{OC_6H_5}$  melting point 90°-91° C. soluble in ether, benzene, or hot alcohol.

*Dyeing*.—505,088, September 19, Bracewell, J., process of fixing colors upon cottons.

*Glue*.—505,615, September 26, Tessen, E., elastic glue or gelatine; made by heating and saponifying with caustic potash and then adding dry magnesium chloride and potash soap. 505,618, September 26, Vogel, B. W., glue for card board; a paste of starch with iodine in solution admixed.

*Plasters and Cement*.—505,747, September 26, Breinig, G. M., artificial stone; crushed quartz, ground calcined quartz, and hydraulic cement are used. 504,933, September 12, Moore, E. A., composition for architectural purposes; consisting of sand, raw gypsum, calcined gypsum, quick lime, glue, sulphuric acid, and kerosene oil. 505,082, September 19, VonAinbach, F. F., artificial stone; composed of powdered and burnt magnesite and a solution of tungstate of soda. 504,477, September 5, LeFevre, C. F.,

cement; borax, twenty-five per cent.; rosin, twenty-five per cent.; glue, fifty per cent., are the ingredients named.

*Miscellaneous.*—505,303, September 19, Withers, S., marbleizing metal, china, etc. 505,576, September 26, Scharling, J. H., depositing layers of metal on glass. 505,520, September 26, Guttman, O., apparatus for concentrating liquids. 505,141, September 19, Tausk, B., process of treating feather fur. 504,774, September 12, Craney, T., electrolytic cell. 505,125, September 19, Pollak, C., electrodes; made from pulverized lead carbonate with caustic soda, or potash added to form a paste. 504,584, September 5, Hunt, A. E., refractory brick; which consists of bauxite bonded with a little lime. 504,388, September 5, Johnson, A., grinding emery wheel; emery, shellac, and salt are incorporated together. 504,724, September 12, Greiner, A. J., composition for preserving food; "charcoal, sulphur, sugar, corn starch, beeswax, saltpeter, cayenne pepper, and ginger." 505,137, September 19, Stebbins, J. H., Jr., process of treating butter. 505,311, September 19, Grindle, P. S., composition for kindling fire; 3 parts sawdust, with 1 part rosin, to which is added  $\frac{1}{8}$  part of combustible cement containing  $2\frac{1}{2}$  parts coal tar,  $1\frac{1}{2}$  asphaltum,  $\frac{1}{2}$  part glue, and 1 of starch. 504,988, September 12, Mellinger, J., artificial wood; lime is mixed with a fibrous material and this is treated with a solution of borax, alum, potassium carbonate, zinc sulphate, sodium chloride, and bicarbonate and silicate and lye, molded and subjected to pressure. 504,898, September 12, Weidig, H. P., apparatus for extinguishing fires; liquid carbon dioxide, into which is injected ammonia, is used for the solution. 504,772, September 12, Arnold, E. and R., composition for lithographic stone; "potassium binoxalate, pumice stone, alum, magnesium chloride, strong sulphuric ether, and water." 505,426, September 19, Steiner, S. W., non-conducting composition for steam pipes; "vegetable, animal, or mineral fiber, and hydrate of lime." 505,531, September 26, McCook, E. M., composition for roofing; "coal tar pitch, anthracene oil, geyserite, and sand, or gravel."

*Ore Separators, Etc.*—506,976, October 17, Campbell, A. C., ore separator. 506,035, October 3, Darragh, F. D., ore concentrator. 506,591, October 10, Guild, G., phosphate separator. 507,465, October 24, Vale, S. W., amalgamating machine. 505,609, October 10, Seymour, C. E., ore concentrator. 506,751, October 17, Wall, E. A., ore jigger. 507,350, October 24, Bohm, W. D., apparatus for leaching ores. 507,204, October 24, Bird, E. J., limestone, or metallurgical furnace. 507,460, October 24, Simonds, G. F., metallurgical furnace. 507,031, October 17, Nesmith, J. W., blast furnace. 507,411, October 24, Briggs, J., kiln for burning limestone. 505,904, October 3, Neill, J. W., separating molten metal by electro-magnets. 506,129, October 3, Pearce, R., regulating blast in ore-roasting furnace.

*Iron and Steel.*—506,689, October 17, Harvey, H. A., steel rail, containing varying proportions of carbon in different parts. 506,518, October 10, Leibert, O. F., apparatus for casting steel or other ingots. 506,799,



October 17, Sentinella, R. L., metallic flux for refining iron and steel for casting; iron, sodium, sodium chloride and iron chloride are heated in a crucible to a semi-fluid condition, when sodium chloride is added and the heat is increased. 507,082, October 17, Raudnitz, S., protecting iron from rust, by immersing in acid bath containing metallic oxide, then dipping in a hydrocarbon.

*Nickel*.—505,846, October 3, Ricketts, P de P., separation in nickel bearing bodies by immersing in sulphuric acid, adding alkaline sulphates and electrolyzing.

*Copper*.—506,985, October 17, Douglass, J., separation from copper matte, by injecting sulphurous acid in solution containing ferrous chloride in which matte is suspended, recovering insoluble subchloride of copper by chloride of iron, and precipitating silver in matte by copper and copper by iron. 506,966, October 17, Baswitz, C., removing copper from textile fabrics; after dipping them in a solution of vegetable parchment in ammoniacal oxide of copper, and evaporating the ammonia, they are treated with ammonium sulphate and aluminum acetate solution to remove the copper and render the fabrics unflammable. 507,130, October 24, Hoepfner, C., electrolytic separation of metals; cuprous chloride solution is formed and electrolyzed.

*Aluminum*.—507,822, October 31, Lancon, M. H., solder; aluminum, 95 per cent.; copper, 1 per cent.; tin, 4 per cent. 505,864, October 3, Wegner, G. and Gührs, P., coating aluminum and alloys, with a solution of acetous verdigris, oxide of iron, sulphur, and ammonium chloride and heating, finally painting with sulphur dissolved in turpentine and firing, and then steeping in bath of linseed oil and brushing the surface with beeswax.

*Acids and Alkalies*.—507,895, October 31, Farmer, J., acetic acid manufacture. 506,029, October 3, Barrows, J. F., burning limestone. 507,741, October 21, Luhmann, E., apparatus for carbonic acid. 507,741, October 31, Luhmann, E., process for carbonic acid manufacture; liquors are heated to expel carbonic acid, and boiled under high pressure in closed boilers to concentrate lye. 506,639, October 10, Knietsch, R., liquid chlorine; passing confined body of chlorine through heated sulphuric acid in a confined space. 507,039, October 17, Rossbach, H., condenser for ammonia. 507,331, October 24, Salomon, F., process for obtaining hydrogen and carbonic acid gas; impregnating carbonaceous material with an alkaline hydrate and passing water vapor through mass, and separating gases. 505,809, October 3, Bowman, R. D., apparatus for oxygen. 505,895, October 3, Cuttarr, E. B., apparatus for soda and chlorine by electrolysis. 506,640, October 10, Knietsch, R., package of liquid chlorine-anhydrous. 507,392, October 24, Tatman, B. F., aerating apparatus for carbonating liquids. 507,753, October 31, Playfair, D. J., process of making cyanides; a sulphocyanate is heated with a metal, whereby an insoluble sulphide and a cyanide, is formed.

*Sanitary Chemistry.*—507,264, October 24, Eickershoff, J. H., filtering and sterilizing apparatus. 507,774, October 31, Ball, P., apparatus for purifying water. 505,967, October 3, Sprague, A. V. M., sterilizing apparatus. 506,248, October 10, Opperman, G., purifying water by electrolysis. 506,879-880, October 17, Jewell, J. H., apparatus for and method of purifying sewage; the sewage is filtered through combustible filtering medium, and separated solids are ignited with this filter. 507,084, October 17, Trillat, J. A., preserving food, by impregnating with formaldehyde.

*Bleaching and Dyeing.*—507,404, October 24, Bentz, E., *et al.*, apparatus for and process of bleaching; the goods are saturated with the bleaching liquor and steamed, while the air is excluded. 506,918, October 17, Kothe, R., *et al.*, blue triphenylmethane dye. 506,265, October 10, Schmidt, R. E., alizarinhexacyanine dye, yellowish brown. 506,284, October 10, Ulrich, M., and Baumann, J., blue tetrazo dye. 506,663, October 17, Bloede, V. E., dyeing black, violaniline and vegetable yellows, such as fustic, with suitable mordants are used.

*Tanning.*—506,696, October 17, James, J. H., tanning process. 507,213, October 24, Chase, J., artificial leather; from animal material by disintegrating in presence of water and reuniting elements under pressure.

*Explosives.*—507,279, October 24, Leonard, M. E., smokeless powder, nitroglycerol, gun-cotton, lycopodium, a "neutralizer of free acid, such as urea crystals or dinitrobenzol and oil" are the ingredients. 506,784, October 17, Kranz, A., dynamite made from nitroglycerol, camphor, and gun-cotton, with linseed oil and oil of turpentine, treated with ammonium nitrate and sulphuric acid. 506,032, October 3, Blomén, J. E., blasting compound; "granules of an oxidizing agent, covered by films of a mixture of a hydrocarbon and dinitrophenol. 506,031, October 3, Blomén, J. E., a hydrocarbon is treated with nitric acid, then with nitric and sulphuric acid, again with nitric and finally with an oxidizing agent.

*Oils and Varnishes.*—507,586, October 31, Ling, E. E., oil solvent; a compound of sodium, lime, and glycerol. 507,749, October 31, Paget, L., pyroxylin solvent; an ozonized menstruum. 507,964, October 31, Borgmeyer, C. L., and Paget, L., pyroxylin solvent; aceto-acetate of amyl, ozonized fusel oil, wood alcohol, and benzine. 507,230, October 24, Laird, R. H., deodorizing and refining crude oils. 507,441, October 24, Koehler, H., refining petroleum, by passing through heated lime. 507,512, October 24, Victorson, V., method for finishing surface of wood; a varnish rich in an oxidizable oil is used, and the wood is heated to evaporate solvent of varnish and oxidize and harden the oil.

*Plaster and Cement.*—507,745, October 31, Moore, C. M., fire and water-proof paint and cement; "brick-bat clay, hard wood ashes, fine sand, common salt, alum, and linseed oil," form the compound. 507,662, October 31, Ménégat, N. D., non-conducting and water-proof cement; made from white clay, yellow ochre, iron filings, cocoanut fiber, wool, flour, charcoal,

and lubricating oil. 506,870, October 17, Carey, P., fire proof covering for steam pipes; consists of asbestos fiber, sulphate of lime, soluble glass, water, and Glauber's salt. 506,356, October 10, Bedbury, G. W., composition for water pipes; contains asphaltum, pulverized clay, magnesia, and asbestos. 506,745, October 17, Stanley, W. L., adhesive compound for metallic coverings; "coal-tar pitch, gum asphaltum, crude rubber, alum, and whiting." 505,916, October 3, Hoffman, J., insulating compound; asbestos fiber with a binder of asphaltum, beeswax, and shellac. 507,678, October 31, Fanning, J. J., insulating compound; contains plaster of Paris, asbestos, dextrin, and linseed oil. 507,942, October 31, Stafford, B. D., composition for plaster; borax, alum, wheat flour, sugar, and slaked lime are claimed. 506,847, October 17, Frear, A. H., artificial stone; an aqueous saccharine solution of litharge, an alkaline solution of shellac, an aqueous solution of glue and ochre, hydraulic cement, sand or gravel, gypsum, and a metallic oxide ore combined.

*Miscellaneous.*—507,473, October 24, Bazille, J. A., and Partridge, G. W., cleaning compound; of flour, sal-soda, olive oil, blue vitriol, venetian red, and water. 506,493, October 10, Hall, F., preserving wood; by immersing in a hot solution containing to each cubic foot of water, 1½ lbs. caustic soda or potash, 4 lbs. soda ash, ½ lb. arsenic sulphide, dissolved in sodium sulphide. 506,109, October 3, Gerland, F. J. M., half-tone negative. 505,983, October 3, Marfori, P., iron albumen preparation; an iron derivate of albumen, containing ten per cent. of iron, soluble in strong tartaric acid, but not in water. 507,969, October 31, Cleaver, J. B., anti-friction composition; plumbago, silk particles, and a fatty substance are used. 507,970, October 30, same patentee, particles of hides or skins are used in place of the silk. 505,847, October 3, Rochow, B., medicinal soap; made from pure tallow soap, white wine, unsaponified olive oil, camphor gum, oil of rosemary, and oil of lavender. 506,004, October 3, Grünwald, J., soap; magnesium chloride, starch, caustic potash, hydrated lime, and glycerol, are the ingredients. 507,246, October 24, Spiceker, G., blocks of fuel; finely divided combustible material and resinous pitch. 507,225,–507,501, Jones, W. H. L., and Warr, G. C., softening vegetable fibres; by the action of boiling glycerol, ammonia, oil, and soap. 506,051, October 3, Langville, L. S., black ash residuum of wood pulp manufacture, treatment of. 505,936, October 3, Bird, H. J., disintegrating vegetable substances; from the paunches of slaughtered cattle.

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### NEW BOOKS.

ANALYSIS OF MILK AND MILK PRODUCTS. BY HENRY LEFFMANN, M.D., PH.D., AND WM. BEAM, M.A., M.D. P. Blakiston, Son & Co. Philadelphia. 1893. 92 pp., 8vo. Price, \$1.

This is the best manual upon the subject of the analysis of milk and its products which has as yet appeared in English.

It is so well brought up to date as to contain notice of work which was published within the month of its own appearance.

Milk itself is treated of under the headings of nature and composition; analytical processes for determination of normal constituents and commercial adulterants; data for inspection, including natural variations and average composition, with standards for basis of official judgment. The sanitary relations of milk are also considered.

The milk products, which are in like manner considered, are condensed milk, butter, and cheese. This portion of the subject, however, is not so satisfactorily covered as is that of milk itself. An appendix contains a table of corrections for temperature in the apparent readings of specific gravity in milk, and for the calculation of the total solids, based upon the gravity and fat separately determined.

The authors have endeavored in this work to provide methods of analysis suitable not only for the professional chemist, but also such as may be safely employed by dairymen and others unskilled in general analytical work. To further uniformity they have included methods which have been agreed upon by the Association of Official Agricultural Chemists of the United States, and which have been published in the *Bulletins of the U. S. Department of Agriculture*. They have also taken freely from *The Analyst*, the official organ of the Society of Public Analysts of Great Britain.

But few exceptions can be taken to the methods of examination which they have recommended in this work. That the watering of a milk, however, can be determined by the increase of the sulphates present as mentioned upon page 19 is hardly warranted. That the fable of milk being sometimes adulterated with calf's brain should be again repeated after the history of that myth had been exploded in the well-known work of Blyth upon "Foods" is surprising, but is only another illustration of the great difficulty of correcting a false tradition when once it gets into circulation.

A few errata are to be noted in the work. There is an evident clerical error in the composition of sow's milk upon page 11, while some of the others are not in accord with the best

authorities. The decimal point should be moved one place further to the right in the fat of skimmed milk on page 14, and in the percentage of fat on page 20. The recommended forms of spelling chemical terms as published by the American Association for the Advancement of Science, have been followed in the work. Its print and paper are good and it will no doubt be widely used.

B. F. D. .

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## PROCEEDINGS.

### MINUTES OF THE BOARD OF DIRECTORS OF THE AMERICAN CHEMICAL SOCIETY.

JANUARY 19, 1893.

THE Board of Directors met in the office of A. A. Breneman, 97 Water street, New York. Present: Messrs. Austen, Breneman, Chandler, Doremus, Hale, McKenna, McMurtrie, Sabin, and Woodman.

Meeting called to order by the secretary at 4.40 P. M., and C. F. Chandler chosen chairman.

F. E. Dodge, librarian, A. A. Breneman, and Morris Loeb were appointed a committee to investigate thoroughly the condition and needs of the library and to make a report to the Board of Directors with such recommendations as they may deem best.

The directors then took up the consideration of by-laws for the society, recommending certain modifications and additions to those now before the council.

Other matters of interest were informally discussed, and the meeting was then adjourned.

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MARCH 4, 1893.

The meeting of the Board of Directors was held in the law lecture room of the University of New York, being called to order at 10.10 P. M., Vice President A. H. Sabin in the chair. There were present: Messrs. Breneman, Doremus, Hale, McKenna, McMurtrie, Sabin, and Woodman.

The treasurer of the society was authorized to remit to the Cincinnati section that portion of their dues for the year 1892 to which they were entitled by the constitution, just the same

as though application had been made for the amount during the year 1892.

The death of Prof. F. A. Genth, an ex-president of the society, was announced, and it was recommended that the secretary communicate informally with the bereaved family to evince the active sympathy of the directors pending any official and formal action that might be taken at a later date.

After some informal discussion the board adjourned.

APRIL 13, 1893.

A meeting of the Board of Directors was held in the office of A. A. Breneman, 97 Water street, New York, April 13, 1893. Present: Messrs. Breneman, Dodge, Doremus, Hale, Leeds, McKenna, Sabin, and Woodman.

The meeting was called to order at 4.30 P. M., Prof. A. H. Sabin, vice president, in the chair.

The Committee on the Condition and Needs of the Library reported with the following recommendations which were adopted by the board, *viz.* :

That the authorities of the University of the City of New York be allowed to remove to different locations in the building at their own expense certain of the society's books and pamphlets in accordance with their request.

That the Library Committee be allowed a sum of money not to exceed fifty dollars for binding back numbers of journals and periodicals.

Mr. F. E. Dodge, librarian, presented to the society four volumes of the *Berichte* of the German Chemical Society, which by a vote of the Board of Directors were accepted with thanks to the donor.

The secretary presented an application by ten members of the Washington Chemical Society for the incorporation of that society as a local section of the American Chemical Society.

After discussion the following resolution offered by A. A. Breneman was adopted :

*Resolved*, That the Board of Directors authorize the issuing of a charter to the ten members of the American Chemical Society residing in or near Washington who have already applied for the admission of the Washington Chemical Society as a section, provided that the said application be so altered in form as to ask directly for the establishment of a local section of the American Chemical Society in Washington.

The board then adjourned.

JUNE 8, 1893.

A meeting of the Board of Directors was held in the laboratory of Professor Doremus at the College of the City of New York, June 8, 1893. Present: Messrs. Breneman, Dodge, Doremus, Hale, Hart, McKenna, McMurtrie, Sabin, and Woodman.

The meeting was called to order at 4.45 P. M., Vice President Sabin in the chair. After some informal discussion regarding the Journal of the society, Professor Hart retired.

The board then adopted unanimously the following resolutions:

*Resolved*, That the Chemical Publishing Company, of Easton, Pa., is hereby authorized to print and distribute the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY for the year 1893 in 1,000 volumes at \$1.80 per volume, each volume to consist of twelve monthly numbers of not less than sixty pages; adjustment being made for the January number, of which only 750 copies were printed; the terms upon which this agreement is made being those which were proposed by the Chemical Publishing Company to the Committee on Papers and Publications of the American Chemical Society, under date 4-17-93.

*Resolved*, That the Board of Directors of the American Chemical Society hereby accept the following propositions made to them this day by Edward Hart: (a) That I suspend the publication of my journal with the June number, and for the rest of the year send to my subscribers the numbers of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY instead; the expense of printing, binding, and mailing the additional copies required for this purpose to be defrayed by me. This plan gives my subscribers the society's journal for six months and will doubtless lead to a largely increased membership. (b) That in case the journal of the society shall at any time cease to be published by the Chemical Publishing Company, the American Chemical Society shall then, if I so desire, take all *complete volumes* of the *Journal of Analytical Chemistry* and of the *Journal of Analytical and Applied Chemistry* then in my hands, paying for them at the rate of one dollar (\$1) per volume unbound. The total amount paid shall in no event exceed \$400. It is also understood that if additional copies of any number shall have been reprinted in the meantime such additional copies shall not be included unless the society so desire.

There being no further business the board then adjourned.

ALBERT C. HALE, Secretary.

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**ERRATUM.**—September number, page 513, first line, for "results in any given *surface*," read "results in any given *service*."

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# THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

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## THE CROSS-FERTILIZATION OF THE SCIENCES.

OPENING ADDRESS FOR THE WORLD'S CONGRESS OF CHEMISTS, SECTION  
OF PHYSICAL CHEMISTRY.<sup>1</sup>

BY ROBT. B. WARDER, WASHINGTON, D. C.

**I**T gives me pleasure to take my turn, while introducing the subject of physical chemistry, to welcome our guests from far and near, and to thank you for the interest shown throughout the week.

Science has been defined as *knowledge classified*; and there are philosophers whose special anxiety it is to find pigeon holes duly arranged in rank and file, where the several classes of facts can be stowed away in order like the various genera and species of a fauna or flora. But the boundaries of a science, as of a biological species, can not always be defined. Hybridism in knowledge, as in husbandry, yields offspring of special value. The late Dr. Gray was wont to exhibit the wonderful natural contrivances of the orchids, by which each pistil should not be fertilized by its own pollen, but by that from some other flower. To this habit no doubt is largely due that wonderful development of form and color. The practical stock-raiser or horticulturist, with an ideal sheep, or cotton-plant, or chrysanthemum, in his mind, proceeds to select and unite the parents, combining the several desirable characteristics, so that the product more and more closely approaches his ideal.

So also in the evolution of science, the most striking developments appear in the judicious combination of distinct parents.

<sup>1</sup> Read August 26, 1893.



The new scientific method lay hidden, until mathematical science was joined with the long history of observation. In more recent times a "new science" has arisen, tracing its parentage from the old science of the soil and from physics on the other. The "stratigraphical method of geology," which was read at Madison last year, sought to trace the history of the mountain range, by joining the science of mathematical physics with stratigraphical and geological geology.

It is especially true in the problems of daily life, that conclusions are reached, not belonging to any one line of investigation, but to nearly the whole range of science. A farmer, for example, with one hundred acres of ground, wishes to produce as many pounds of butter as possible. Geology and chemistry to the interpretation of his soil; history is chiefly concerned with his pasture and his herd; physiology and physics deal with the processes of feeding and utilization while the best market for the butter and utilization is determined more primarily to the laws of political economy.

It is likewise in many such illustrations. The manufacturer of the engine can never say of any kind of science, "I will do it in any one science." A life-time may be spent in the study of the history of any one science (if one has leisure for such study), but the most important and fruitful outcome is the product of different sciences.

The reality of such union is especially noteworthy in chemistry and physics. Let us take some examples from the papers of the late Professor Prescott, in discussing the relation of the properties of optical and thermal decomposition of substances, such as solubility, capillarity, etc. He is alive to the new physical chemistry, and is more intelligent than analysts. The same fact is true of the distinguishing properties of olive oil in the laboratory. The proper adjustment of the conditions required in electrolytic separations; the President of American Association for the study of the "Methods of Testing Fats and Oils," by Milliau,

and the speed of chemical action (varying with the temperature) must be responsible for many discrepancies in the estimation of citrate-soluble phosphates.

Passing to organic chemistry, the question introduced by Professor Witt,<sup>1</sup> "Why make so many dye-stuffs?" led us to the absorption (or subtraction) theory of the mixture of pigments, as distinguished from the addition theory, applicable to physical colors. Still more singular is the extension of the theory of solution to cover the nature of dyed wool, silk, or cotton, where the dye must be selected with due regard to its solubility in the fiber to be colored. In this industry, conditions of chemical equilibrium are especially important. Bright colors with a high degree of chemical energy may sell well the first season, but in the end are sure to disappoint all parties concerned.

The scientific and statistical basis for the assessment of farms has been discussed by Professor Thoms.<sup>2</sup> The principles of political economy involved may be referred to those officials who require the farmer to pay more than his share of tax, but the subject of values was seen to be closely linked to both the chemical composition and the physical properties of the soil.

To review yesterday's papers on technological chemistry and to point out all the fruits of cross-fertilization between chemistry and physics, would tax your patience too far. Some of the more striking illustrations are found in the apparatus for rapid removal of latent heat from vapor of nitric acid as described by Dr. Hart;<sup>3</sup> the judicious selection of a solvent for the electrolysis of alumina, and the economical preparation of a disinfecting fluid by electrolysis of sea water<sup>3</sup> as discussed by Professor Langley.<sup>3</sup>

In all the operations and needs of daily life, we find chemical substances adapted to their several purposes in virtue of their physical properties. For many years the discussion of density, solubility, optical, thermal, and electrical properties,

<sup>1</sup> "Artificial Coloring Matters," *this Journal*, 15, 456-463.

<sup>2</sup> Not yet published.

<sup>3</sup> Other industrial applications were presented to the Section of Physical Chemistry in a paper, "On Apparatus for Promoting the Interaction of Liquids and Gases," by Professor George Lunge, *this Journal*, 15, 361-374.

crystalline form, etc., were grouped under the name of chemical physics. A vast store of facts was accumulated, of somewhat empirical character, like a valley of dry bones. A new life has appeared with the recent developments of the doctrine of energy. The old name takes a new form. The old numerical data have been greatly extended with the addition of broad generalizations. Physical chemistry is the order of the day. But what is this physical chemistry? And what is it for?

Nearly twenty years ago, a chemical student in Berlin was using costly organic materials by the hectogram or kilogram to prepare some new compound in quantities barely sufficient for analysis. Looking forward he dreamed of some general laws yet to be discovered by which it might be known whether a given blackboard equation would or would not find its counterpart in the laboratory without the necessity for such expenditure of time and material to prove each point. Are we not to-day somewhat nearer the realization of that dream?

We form a plan and want to know whether it will work. We put it into execution and find it works in part. There are losses, sources of waste, that must be overcome before the process can fulfill our wishes. We now ask, not merely, Will it work? but How far will it work? And this is the very question in its general form which occupied the mind of J. Willard Gibbs about the same time that the student was indulging in his reveries. The result was a paper, "On the Equilibrium of Heterogeneous Substances," a paper bristling with differentials and integrals, with the merit of applying equally to physical and to chemical operations. It presents the fundamental principles of change or non-change in general terms, requiring only the proper application of minor premises to yield the particular facts desired. Experiment is still required to find the minor premise, but rapid progress has been made.

This is abundantly shown by Professor Ostwald's last volume on chemical energy, covering more than 1,100 pages. This distinguished author has very kindly sent us a brief review of the leading principles in the paper next on the program.<sup>1</sup> Sooner or

<sup>1</sup> "On Chemical Energy," *this Journal*, 15, 421-430. The translation was kindly made for the Congress by Mr. Wm. H. Krug.

later this new leaven will doubtless be felt in agriculture, in technology, and in biology. Already we find a special chair of physical chemistry in Cornell University, from which we shall hear further.<sup>1</sup> Other universities may do well to recognize this middle field in fixing the limits of the several professorships. The time is at least ripe for a more general acquaintance with the subject.

## THE COMPOSITION OF AMERICAN CHEDDAR CHEESE.<sup>2</sup>

BY L. L. VAN SLÝKE.

IN the course of a large number of experiments made in the manufacture of cheese at the New York (Geneva) Experiment Station, a careful study was made of the composition of the cheese manufactured. Knowing the composition of the milk and of the resulting cheese, it was possible to trace the influence of the composition of the milk upon the composition of the cheese. The results given are for the green cheese as it came from the press. The composition of the cheese in a cured or marketable condition can be calculated by allowing for a loss of water varying from four to eight per cent. The first thoroughly reliable analyses of American cheese by an American chemist were published by Dr. Caldwell in 1877, but these were not large in number, and the composition of the milk was not given or known.

The points relating to the composition of cheese upon which I desire especially to dwell briefly are the following:

1. Water and solids.
2. Fat.
3. Casein and albumen.
4. Relation of fat to casein in cheese made from normal milk.
5. Relation of fat to casein in cheese made from skimmed milk.
6. Relation of fat to casein in cheese made from milk containing added cream or other fat.

<sup>1</sup> "The Fundamentals of Chemical Theory," by Professor J. E. Trevor, *this Journal*, 15, 430-448.

<sup>2</sup> Read before the World's Congress of Chemists, August 24, 1893.

7. Changes in composition taking place during the ripening process.

#### I.—WATER AND SOLIDS IN CHEESE.

Taking all the cheese made from normal milk during six months the per cent. of water in the green cheese varied from 33.50 to 42.90 and averaged 36.50 per cent. There was a greater variation in water than in any other constituent of the cheese. Our work shows that cheese-makers are far from being able to control the amount of moisture to be retained in cheese. To discuss the question as to how much moisture it is desirable to retain in cheese would take us beyond the limits of this paper. The variation in solids was, of course, the same as that of moisture.

#### II.—FAT IN CHEESE.

The per cent. of fat varied from 30.84 to 37.24 and averaged 34.33 per cent. This variation in fat was caused quite as much by variation in the water retained as it was by variation in the composition of the milk used.

#### III.—CASEIN AND ALBUMEN.

The amount of casein and albumen varied from 22.11 to 26.10, and averaged 24.25 per cent. The amount of albumen retained in cheese from milk is very minute and probably does not exceed 0.10 per cent., so that we might justly speak of the nitrogen compounds contained in cheese as casein alone.

#### IV.—RELATION OF FAT TO CASEIN IN CHEESE MADE FROM NORMAL MILK.

In another paper I have shown that the fat and casein in normal milk bear a fairly definite relation to each other. A similar relation also holds good for cheese made from normal milk. We found that almost without exception cheese made from normal milk contained not less than 1.30 pounds of fat for one pound of casein; the average was 1.42 pounds of fat for one pound of casein, while the ratio does not often drop below 1.35.

#### V.—RELATION OF FAT TO CASEIN IN CHEESE MADE FROM SKIMMED MILK.

Removal of fat from milk influences the composition of cheese in much the same way that it does that of milk. Skimming milk increases the amount of casein relative to the fat not only

in the milk, but also in the cheese made from such skimmed milk. The greater the amount of fat removed from normal milk, the less will become the amount of fat relative to casein in the resulting skim-milk as well as in the cheese made from such skim-milk. In no case did we find cheese made from skim-milk to contain as much as 1.30 pounds of fat for one pound of casein. The nearest any cheese came to this was one made from milk, from which less than ten per cent. of its fat had been removed, and in this cheese the ratio was 1.27. When milk is skimmed before being made into cheese usually not less than one-fourth or one-third of its fat is removed, because it does not pay to remove less than this. In such cases, the cheese contains about equal parts of fat and casein. I feel quite confident that this relation can be made to serve as a basis for the identification of cheese made from skim-milk, and that, in case of cheese made from the mixed normal milk of herds of cows, there will rarely or never be less than 1.30 pounds of fat for one pound of casein, unless the cheese was made from skimmed milk. A well-known author says that a cheese which contains less than ten per cent. of fat may with propriety be called skim. I should say that any cheese is a skim-cheese if it contains less than 1.30 pounds of fat for one pound of casein even if it contained forty per cent. of fat.

VI.—RELATION OF FAT TO CASEIN IN CHEESE MADE FROM MILK CONTAINING ADDED CREAM OR OTHER FAT.

The effect of adding cream or other fat to normal milk is to make the amount of fat larger relative to the casein, and the same effect is produced in the cheese made from such milk, so that there will be 1.70 or more pounds of fat for one pound of casein.

The statement is commonly made that good whole-milk cheese consists of one-third water, one-third fat, and one-third casein. This certainly is a convenient statement to remember, but for accuracy it can not be commended; for I have never yet in my work met with a sample of normal milk of such composition as would make such cheese as the above three-thirds cheese; Such cheese could be made only from partially skimmed milk, if it could be made at all.

To summarize, we found that the composition of green Cheddar cheese as made in our American cheese factories, averaged during the season as follows in round numbers:

	Per cent.
Water .....	36.50
Solids .....	63.50
Fat .....	34.25
Casein .....	24.25
Ash, sugar, etc.....	5.00

Such cheese would have approximately the following composition when it reached the consumer:

	Per cent.
Water .....	31.50
Solids .....	68.50
Fat .....	37.00
Casein .....	26.25
Ash, sugar, etc.....	5.25

#### VII.—CHANGES IN COMPOSITION OF CHEESE TAKING PLACE DURING THE RIPENING PROCESS.

Cheeses were made from milk of varying composition and under certain different conditions; they were analyzed when green and again when five months old. They were kept in a room the temperature of which varied from 60°–70° F.

##### *1st.—Loss of Weight.*

(a) The total loss of weight varied from 10.65 to 17.20 per cent. and averaged 13.53.

(b) The loss of weight was greatest in the cheese which contained, when green, the largest amount of water of any cheese made from normal milk.

##### *2d.—Loss of Water.*

The amount of water lost in five months varied from 8.14 to 14.95 per cent. and averaged 10.60 per cent. This was equivalent to from 20.56 to 34.83 per cent. of the water in the cheese, with an average of 26.58.

##### *3d.—Loss of Solids.*

The amount of solids lost varied from 1.57 to 3.90 and averaged 2.88 per cent. of the cheese; this was equivalent to from 2.50 to 6.80 per cent. of the solids in the cheese with an average of 4.82 per cent.

*4th.—Loss of Fat.*

There was practically no loss of fat.

*5th.—Loss of Casein.*

In every case there was a loss of casein varying in amount from 0.90 to 2.20 per cent. and averaging 1.48; this was equivalent to from 4 to 7.83 per cent. of the total casein present in the cheese, with an average of 6.15 per cent.

*6th.—Changes in the Form of Casein.*

(a) In every case the amount of soluble nitrogen compounds increased very much in five months. In the cheese, when green, the amount of nitrogen in the form of soluble compounds varied from 0.10 to 0.26 per cent. of the cheese and averaged 0.16 per cent., which was equivalent to from 3.12 to 7.19 per cent. of the total nitrogen in the cheese, with an average of 4.23 per cent. At the end of five months the amount of nitrogen in the form of soluble compounds varied from 0.98 to 1.70 per cent. of the cheese, with an average of 1.24, which was equivalent to from 28.57 to 47.33 per cent. of the total nitrogen in the cheese, with an average of 35.52 per cent.

(b) The cheese, when green, contained no nitrogen in the form of amide compounds, while at five months there was contained from 0.26 to 0.50 per cent., with an average of 0.39, which was equivalent to from 7.58 to 13.93 per cent. of the total nitrogen in the cheese with an average of 11.66 per cent.

(c) The cheese, when green, contained no nitrogen in the form of ammonium compounds, while at five months there was contained from 0.078 to 0.126 per cent., with an average of 0.103, which was equivalent to from 2.42 to 3.51 per cent. of the total nitrogen in the cheese, with an average of 2.92 per cent.

(d) The cheese, in the manufacture of which the largest amount of rennet was used, contained considerably more of the soluble nitrogen compounds than did any other cheese when five months old. This would indicate that the amount of rennet used had some influence upon the rapidity of ripening.

(e) The cheese made from partially skimmed milk contained the smallest proportion of soluble nitrogen compounds at five months, while the cheese made from milk containing added



cream contained with a single exception the largest proportion of soluble nitrogen compounds. This would indicate that in cheese rich in fat the insoluble casein is converted into soluble forms more rapidly than in case of skim-milk cheese; in other words, cheese rich in fat becomes digestible in ripening more rapidly than skim-milk cheese.

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**THE PURIFICATION OF WATER, WITH SPECIAL REFERENCE TO BOILER FEED WATERS AND SCALE PREVENTION.<sup>1</sup>**

BY C. A. DOREMUS.

PROF. VIVIAN B. LEWES, of the British Royal Naval College, has epitomized in two papers read before the Institution of Naval Architects in 1889 and 1891 a series of the most highly interesting and instructive analyses and experiments on incrustations in marine boilers and their causes to be found in the literature relating to scale formation.<sup>2</sup> A careful study for some years of a great variety of boiler feed waters from all sections of the country has convinced me that many points brought forward by Professor Lewes are so generally applicable that they can not be overlooked by the chemist who attempts to rectify the serious troubles arising from these sources.

The following quotations are typical: "The presence of calcium sulphate exercises a very marked influence upon the condition and physical properties of the incrustation as under the conditions in which it is formed in a boiler it separates in a crystalline form and binds the deposit into a hard mass, an action which is also aided by the presence of magnesium hydrate." When calcium sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcium sulphate and one of water; whilst after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a further change of crystalline form, and becomes "anhydrite, which is pure calcium sulphate free from

<sup>1</sup> Read before the World's Congress of Chemists, August 25, 1893.

<sup>2</sup> *Chemical News*, 59, 222, and 63, 191.

water of crystallization, and it is this change in crystalline form which binds deposits containing it into such a hard mass."

In many carbonated waters the calcium carbonate also forms upon the heated surface as a crystalline coating, even though the quantity in solution is trivial. Thus in a Croton water which carries but a grain or two per gallon a scale forms on all heated surfaces, tubes as well as crown sheets, which is distinctly crystalline. The massive concretions often found in feed water heaters are crystalline in structure and firmly adherent to the hot tubes or surfaces. It is very easy to show this by a simple experiment. Place a carbonated lime water in a beaker. Raise it to boiling by steam delivered into it by a glass tube. The latter will become coated with an adherent crystalline layer of calcium carbonate. With gypsum water the incrustation does not form so readily since calcium sulphate is soluble to some extent in boiling water, and thorough precipitation not taking place before  $140^{\circ}$  to  $150^{\circ}$  C., a state of affairs reached in practice in boilers, where the calcium sulphate then separates in a crystalline form and attaches itself to the rough heated metal.

In a paper read at the Newport meeting I called attention to the use of sodium fluoride as an agent hitherto overlooked in water purification. Since then I have had opportunities to get the results of its use in several lines of work, but the present paper will be restricted to the service this substance renders in scale prevention. Starting with the idea that is so prevalent, that successful treatment of feed waters should be accomplished by such chemical or mechanical, or combined chemical and mechanical treatment, that the incrusting salts should be removed previous to the water entering the boiler, it was soon seen that this theoretical ideal was not practicable. There are many waters which yield an incrustation, whose proportion of lime and magnesium salts is so small that precipitation can not be effected either by the use of feed water heaters or of chemicals. Yet such waters yield a crystalline scale and often a scale containing magnesium hydrate. Surface condensers are frequently leaky, and many marine boilers starting with good water acquire scale from this cause. Manifestly such waters

can only be treated by chemical means in the course of concentration in the boilers. From these almost soft waters we pass by upward grade to the excessively hard, which can be purified in some measure merely by heating or by chemicals. Since, however, calcium sulphate is not completely precipitated at  $100^{\circ}\text{C}$ ., feed water heaters do not remove it thoroughly enough to prevent scale, and where waters have a permanent as well as temporary hardness due to magnesium salts these are not eliminated. When lime, soda ash, or caustic soda, or a combination of any of these is made use of, it is difficult to regulate the amount required to effect so complete a precipitation that no scale will form, and the trouble attendant on this style of purification is so great that in many cases it has been abandoned. Water softened by lime and soda ash or treated by soda ash or caustic, will generally possess an alkaline reaction, and is, for some purposes therefore unserviceable. The chemical treatment frequently causes the lime salts to separate in crystalline form, large masses of great thickness being formed.

In one instance the feed pipe for a battery of boilers, though five inches in diameter, became so incrustated that a one-inch bar could not be thrust through it. The water had been treated with soda ash and afterwards filtered.

At an artificial ice factory using hard well water the sand of the filter became hard as stone from the calcium carbonate which crystallized upon it even after the water had been treated with soda ash and heated to soften it.

The cost of chemical treatment is often a bar to its employment quite aside from the expense of accessory apparatus, as settling tanks, filters, etc., since to be effective at least the theoretical quantity of precipitant must be used, with soda ash two or three times this quantity.

When sodium fluoride is added to water containing even a very moderate proportion of lime or magnesium salts a precipitate forms at once. When added in quantity sufficient to unite with all of the calcium and magnesium to form fluorides of these metals and the water is then boiled down the precipitate retains its amorphous character. Viewed through the microscope, it has always been found powdery and rounded. This circum-

stance together with other considerations has led to the employment of sodium fluoride in the direction of scale prevention, and it is pleasant to be able to record that to-day it is in successful operation in nearly every section of the country.

It is not an uncommon practice abroad<sup>1</sup> to employ sodium carbonate directly in the boiler, transforming the calcium sulphate to carbonate. The conversion not only of the sulphate of calcium but all magnesium salts to pulverulent fluorides therefore seemed possible and has proved practicable. Calcium fluoride has a molecular weight about twenty-five per cent. less than either calcium carbonate or sulphate or an equivalent quantity of phosphate and therefore the precipitate or sludge formed through its use is much more manageable and removable by blowing down the boilers.

At first it was deemed necessary to determine the total calcium and magnesium of the water often to make a sufficiently complete analysis to determine the salts held in solution and to calculate from these data the quantity of sodium fluoride necessary to transform the calcium and magnesium to fluorides.

Carefully made tests have shown, however, that in the greater number of instances a quantity of sodium fluoride one-quarter of this theoretical amount will, if fed continuously, prevent the formation of scale and leave the interior surface of the boiler so smooth that one chief cause of crystals attaching themselves is done away with.

The various types of water from New York to Albany and from there through the salt district to the lakes at Buffalo are now under this treatment with entirely satisfactory results. The employment of so small an amount of the chemical naturally reduces the cost of purification, while the ease of handling pleases the engineer.

More than once it has happened that the boilers were heavily incrustated when the use of the fluoride was begun. The old scale was found to loosen rapidly, falling off in some cases by the bucket full. In others it was rotted and softened so that on the first cleaning it was easily scraped off.

\* A specimen of highly silicated scale is presented to show how

<sup>1</sup> L. Vignon, *Bull. Soc. Chim.*, III, 2, p. 596.

a chemical transformation with the formation of fluoride has resulted from the continued action of small quantities of sodium fluoride added to the feed water. When once thoroughly cleaned to the metal new scale does not form in such instances.

Live steam is so frequently used now in our large manufacturing establishments for cooking, boiling, etc., and so much condensed steam is used to furnish distilled water, especially in artificial ice manufacture, that a method of treating boiler water in such a way as to furnish pure untainted steam is exceedingly desirable. Since sodium fluoride completes its work without rendering the water alkaline the steam from water thus treated has proved most excellent for such purposes.

It is beyond the province of this article to enter more fully into these details.

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### IMPROVED APPARATUS FOR THE VOLUMETRIC DETERMINATION OF CARBON DIOXIDE AND OTHER GASES.<sup>1</sup>

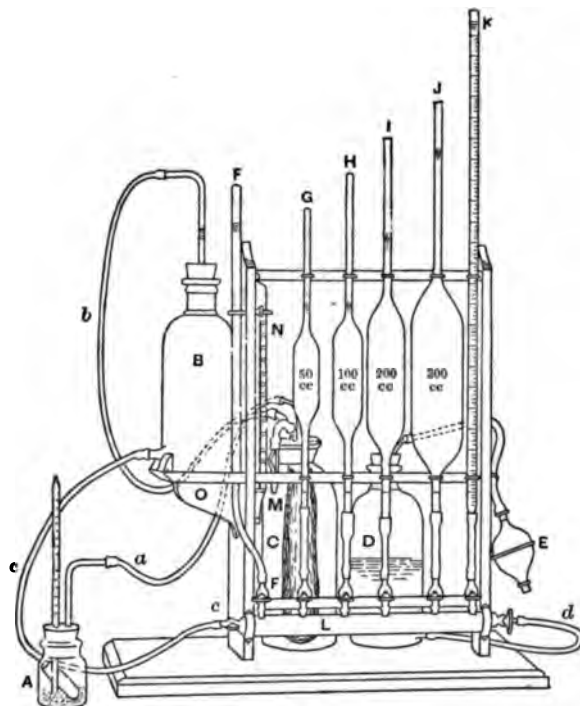
BY CHARLES A. CATLIN.

FOR the determination of small quantities of carbon dioxide in readily decomposed carbonates, the process and apparatus devised by Dr. Scheibler presents a most convenient and rapid method; but the inability to thus measure large quantities of gas has restricted its employment for the most part to determination of carbonate in bone-char. To extend the field of volumetric carbon dioxide determination I have devised the following described apparatus, retaining, as far as possible, the essential features of the Scheibler.

Referring to the cut: A, C, and D are essentially the same as in the Scheibler apparatus, A, being the decomposing bottle in which the portion of the sample to be operated upon, is placed, with its enclosed tube for the decomposing acid or other solution, with the further addition however, of a thermometer, inserted through the rubber stopper—a most important feature when the decomposition results in wide variations of temperature; C, the bottle containing the rubber gas balloon connected

<sup>1</sup> Described at June, 1893, meeting of the Rhode Island Section of the American Chemical Society.

with A, and D the water reservoir with compressing bulb E, exactly as in the Scheibler device. In the Scheibler apparatus however, the volume of the gas evolved is directly determined by the displacement of water in a graduated tube, the capacity of which is, and must be, quite limited.



In my apparatus I have replaced this graduated tube by the bottle B, connected by the tube *b* with the space around the rubber bag in the bottle C, and by the tube *c* from its bottom, through the stopcock, with the tube L, which tube L connects, through another stopcock at its opposite end, with the reservoir D, by means of the tube *d*. This tube L, which may be constructed of brass if more convenient, is fixed horizontally upon the standards, as shown in the cut, and has affixed along its upper portion, a series of stopcocks, one of which connects with the tube F, and each of the others individually, with the pi-

pettes G, H, I, and J,\* and the burette K. These pipettes may be respectively (using a fifty cc. burette for K) 50, 100, 200, and 400 cc. capacity, graduated as to contents, between marks on the stem and delivery tube, in each case. The tube F serves as an equalizer of pressure, as hereinafter described. N shows a common tube thermometer attached to the standard for convenient reference.

Before using the apparatus, the reservoir D is supplied with water, and by means of the compressing bulb E, the burette and pipettes are filled to their zero marks, and their respective stopcocks closed, the stopcocks connecting *c* and F being closed meanwhile. The stopcock connecting *c* is now opened, and the bottle B filled a little above a zero mark upon the tube *b*, which for a portion of the way is of glass; this glass tube being so inserted in the rubber stopper that the bottle may be entirely filled with water without air space. During the filling of B, the stopcock M should be opened, connecting as it does with the air space surrounding the gas bag within the bottle C, while the generating bottle A should be disconnected and the gas bag collapsed. When B is filled, the stopcock connecting it with L is closed, and that at F opened, and this tube filled in like manner to a point higher than the zero mark of B, when the stopcock connecting *d* is closed, and that at *c* opened again. The generating bottle A with its charge of sample and acid in the tube, is now connected, and through the stopcock connecting *d* the level of the water in B adjusted to the zero mark, that in F subsiding with it. When the adjustment is thus effected, the stopcock connecting F, and that at M are closed, while that connecting with the reservoir through *d*, is opened, and thus free course given for the water between B and D. The bottle B being elevated upon the shelf O, there is of course a reduction of pressure within the apparatus, causing a subsidence of the water level; which after a few moments should cease, showing that the apparatus is tight in every joint. If, however, this is not the case, and the level continues to subside, there is a leak, which must be corrected and a readjustment of pressure effected before the operation is continued.

\* By an error of the engraver this pipette is marked 300 cc. It should be 400 cc.—ED.

When all is in readiness, the decomposition of the carbonate is effected in A by bringing the acid and carbonate together in the usual way, the temperature having been noted at the outset. The evolution of the gas, distending the rubber gas bag, expels a portion of the air from C, which forces the water from B into the reservoir D, in volume equivalent to the gas evolved at the pressure and temperature prevailing, as is readily understood. When complete decomposition is effected, and the temperature in A returns to the temperature of the room, by means of the bulb E, pressure is exerted upon the reservoir D, and the stopcock connecting F being opened, the levels in B and F are brought together through the stopcock connecting *d*.

When this is accomplished, the stopcocks at F and *d* are closed. It is seen that the displacement of the water in B obtained in this manner is exactly that of the volume of the gas evolved from the carbonate at the existing temperature and atmospheric pressure. With all stopcocks closed, excepting that connecting *c*, and that at M which should now be opened, the bottle B is removed from its shelf to the table upon which the apparatus stands, and the amount of the displacement measured by running in the contents of such of the pipettes, and portion of the contents of the burette, as may be required to restore the water level in B to the starting point, the amount of water thus employed of course being that measure.

From the volume of gas obtained, the percentage by weight of the sample taken is calculated in the usual way, either by the formula for correction of volume for temperature and pressure, adding of course to the volume thus obtained a correction for carbon dioxide dissolved in the decomposing liquid, or through the use of the tables given originally by Dietrich, (*Ztschr. anal. Chem.*, 4, 141). It is to be noted, however, that these tables are not strictly correct, the weight of the cubic centimeter of carbon dioxide at 0° C. 760 mgms. being considerably at variance with that at present given by the best authorities, and some slight errors, in the calculation apparently, are also to be observed. In ordinary work, however, these are not important. But in the use of the table given for solubility of the gas in the decomposing acid, one must exercise no little caution. In fact



for this correction, it is better to establish for one's self just what it should be for each material operated upon, by check gravimetric determinations; for while within limits this may be taken as a constant factor, yet it is more or less affected by the character of the salts present. And further, this table was not carried far enough to cover the large volumes of gas evolved from the charges that my apparatus enables one to employ.

With this apparatus it is possible to make a determination of carbon dioxide in from ten to fifteen minutes, and that with extreme accuracy. Indeed with the large charges one may employ, and with careful weighings, repeated results obtained from the same sample, will never vary more than one-tenth per cent. and scarcely more in most instances than two or three one-hundredths per cent.

### ARE PENTOSE FORMED BY THE ASSIMILATION PROCESS?<sup>1</sup>

DR. G. DE CHALMOT, AGRICULTURAL DEPARTMENT, RICHMOND, VA.

**I**N recent years the chemistry of the sugars having been revolutionized by the investigations of Kiliani, Fischer, Tollens, and others, the study of the assimilation process, by which the carbohydrates in the plants are originally formed, has also received a new interest.

The theory of Bayer, according to which the first product of the assimilation is formaldehyde, has recently received a very strong support by the results which Bokorny obtained.<sup>2</sup>

Fischer observed some years ago that glyceric aldehyde was probably an intermediate product in the assimilation process, since it most readily unites with itself, yielding hexoses, when placed under proper circumstances.<sup>3</sup>

Pentosans, substances which yield pentoses by hydrolysis, are most widely distributed in plants and form often a large part of their dry matter.<sup>4</sup> The pentoses, xylose, and arabinose, belong to the laevo series (of Fischer) in contrast with the more

<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

<sup>2</sup> *Ber. d. bot. Ges.*, 9, 4, 103.

<sup>3</sup> *Ber. d. chem. Ges.*, 23, 2238.

<sup>4</sup> *Am. Chem. J.*, 15, 21, note.

widely spread hexoses, glucose, and laevulose, which belong to the dextro series.

From a chemical point of view it is more likely that the laevo-pentoses and dextro-hexoses are formed beside each other by the assimilation process, than that they are formed out of each other. The theory of Bayer thereby admits just as well the formation of pentoses as that of hexoses. On the other hand, strong support will be given to Fischer's theory that glyceric aldehyde is an intermediate product, if it be proved that the pentoses in plants are not formed by the assimilation process. I have, therefore, investigated this subject, and I have reached results which prove that pentoses are not formed by the assimilation process unless in imperceptible quantities. Let us see how this result was obtained.

Of the methods used for the quantitative analysis of the pentoses I can only say a few words. Pentoses yield, as is well known, about fifty per cent. of furfural when heated under proper circumstances with dilute hydrochloric acid. Upon this property the methods for determining pentoses are based, since they vary only in the way in which the furfural is estimated.

Two different methods were used. When larger quantities of pentoses are present, I used the method of Tollens and myself with the alterations recently proposed by Tollens and Flint. By this method the furfural is precipitated and weighed in the form of hydrazone. This method when properly executed gives very accurate results. If only very small quantities of pentoses are present in solutions, the furfural is determined by a colorimetric method making use of its property of yielding a red dye-stuff when mixed in an acetic acid solution with an alcoholic solution of anilin oil in the absence of free mineral acid. This method was published in the American Chemical Journal of this year.<sup>1</sup> Since hexoses also yield small quantities of furfural when heated with hydrochloric acid, for examples, fructose (0.2 per cent.), glucose, and galactose (0.04 per cent.) it is necessary to determine also the total amount of sugars if only very small quantities of furfural are obtained, in order to be sure that pentoses are present. I considered that the pentosans known

<sup>1</sup> *Ibid.*, 15, 25 and 277.

to exist in plants are insoluble in water and can not, therefore, be removed as such. As it is a matter of course that if the pentoses are formed in the leaves they must migrate to other parts of the plants, since we find them there, I looked for easily soluble pentoses. I therefore made extracts of the parts to be investigated by immersing them in water, and was able to trace in the leaves of thirty-five plants belonging to widely different families and also in the colorless bark soluble pentoses.<sup>1</sup> I concluded that soluble pentoses occur universally in green higher plants.

These soluble pentoses diffuse readily through membranes permeable to water, as parchment paper and parchment. They furthermore do not diminish perceptibly in dying leaves. For these reasons the soluble pentoses are true transport substances. They are, however, present in much smaller quantities than the soluble hexoses. The largest amount found was 0.4 per cent. in the leaves of *Tecoma radicans*. In many instances the amount does not exceed 0.05 per cent.

If the pentoses are formed by the assimilation process, they are either removed as soon as they are formed or they are temporarily stored, probably in an insoluble form and gradually removed. If the pentoses are removed as soon as they are formed, there ought to be much more soluble pentoses in the leaves during the time of the assimilation than after that time. I therefore collected of the sycamore and the oak the same surface of leaves at half-past four and ten o'clock in the morning and at five and nine in the afternoon. The oak leaves contained at sunrise slightly less soluble pentoses than at other times of the day. In the sycamore leaves I could not perceive any difference. The pentoses are therefore not as quickly removed as they are formed, a fact which was probable from the beginning. I made nine investigations of oak leaves and found in seven instances slightly more soluble pentoses in the evening than at sunrise. In one instance the leaves contained less soluble pentoses in the evening, but then the specimens of morning and evening leaves did not exactly agree. A small difference seems therefore evident, a

<sup>1</sup> *Ibid.*, 15, 21.

difference amounting to from 0.01 to 0.02 per cent. of the weight of the fresh leaves. In leaves of other plants I have not been able thus far to detect the same difference. I therefore concluded that the pentoses are temporarily precipitated in the chlorophyl grains and gradually removed. In the oak leaves the pentoses assimilated during the previous day should be nearly or fully removed at sunrise.

The idea that the pentoses are temporarily precipitated mixed with hexoses as starch of assimilation is not so improbable since Winterstein found pentosans which are soluble in boiling water and give a blue color with iodine.<sup>1</sup> Moreover, I was able to prove that the insoluble pentosans in seeds are resolved during the germination and removed into the germs. Notwithstanding all this, this hypothesis is wrong, as I have proved beyond doubt that no such accumulation of pentoses in the leaves takes place.

If pentosans are transported to any extent out of the leaves during the night we will find that a certain surface of leaves collected in the evening contains more pentosans than a closely similar surface of exactly the same size collected in the morning. If, on the contrary, no such transportation takes place we will find no difference, and since a certain amount of dry matter is transported out of the leaves during the night we will find that the dry matter in the leaves contains a smaller percentage of pentosans in the evening than in the morning.

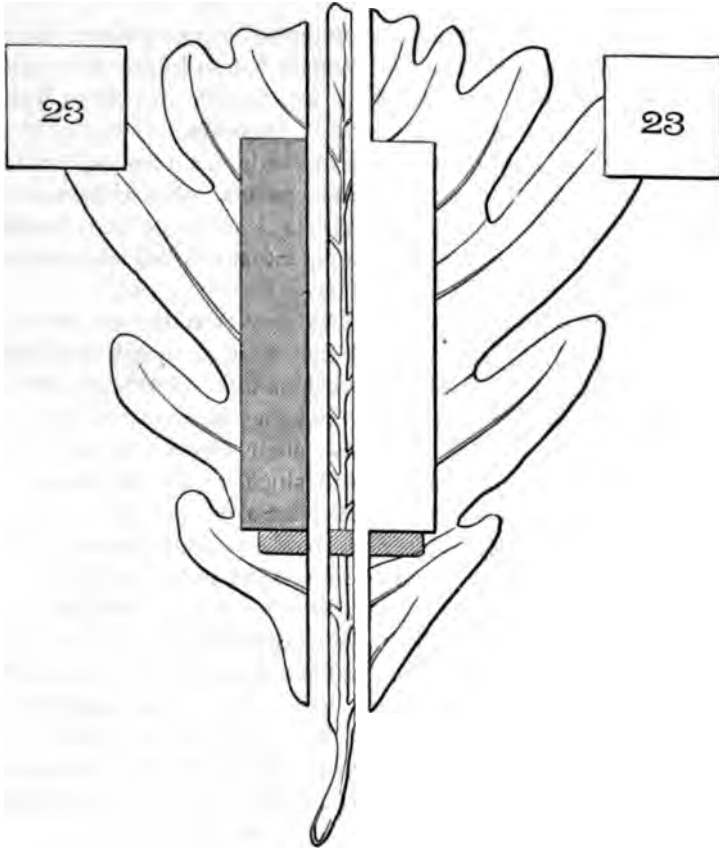
For these investigations I used the method of leaf halves of the German physiologist, Sachs,<sup>2</sup> and collected my specimens as indicated in the drawing. I number from 70 to 100 leaves, attaching with varnish on both halves the same number. I make on the lower part of each leaf also with varnish a little mark across the mid-rib. At seven o'clock in the evening I sever a piece from every leaf by cutting close to and parallel with the mid-rib. Out of each of these pieces I cut with a razor a strip the form of which is given by a piece of iron plate. This is applied with one of its long sides along the cut, and with its lower end touching the mark. Each strip receives the

<sup>1</sup> *Ber. d. chem. Ges.*, 25, 1237.

<sup>2</sup> *Vorlesungen über Pflanzenphysiologie*, 304.

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same number as the leaf from which it is derived on a strip of paper which is wrapped around it. The strips of leaves are then quickly dried at  $100^{\circ}\text{C}$ . The next morning at half past three I collect, number and dry the symmetrical strips of the other halves of the leaves. The numbers of strips of both series are then compared and those strips taken out of which the



counterpart fails, which will sometimes happen, since one of the times of collection is before sunrise. The difference in weight of both lots of dried strips gives very accurately the total amount of dry substance removed during the night or stored during the day in the case in which I collect the first lot before

sunrise and the second in the evening. The dried strips are then pulverized and exactly the same quantity of each taken for the estimation of the pentoses. Both analyses are made side by side and with the utmost care. I have put together in the following table the different results obtained :

	Evening.		Morning.		Total amount of assimilation products stored in 1 sq. meter of leaves.	Excess of pentosan in 1 sq. meter [of leaves in the] morning.	Excess of pentosan in 1 sq. meter of leaves in the evening.
	Weight of 1 sq. meter of leaves.	Per cent. of pentosan.	Weight of 1 sq. meter of leaves.	Per cent. of pentosan.			
	gms.	gms.	gms.	gms.	gms.	gms.	gms.
Corn (Zea Mays) I .....	33.456	14.49	28.633	17.26	4.823	0.098	.....
II .....	35.354	15.35	31.644	17.21	3.710	0.018	.....
Oak (Quercus alba) I ...	70.343	6.77	66.977	7.16	3.366	0.030	.....
II ...	57.906	7.86	55.493	8.30	2.413	0.060	.....
Tropaeolum majus.....	26.143	4.01	23.401	4.42	2.742	.....	0.014

Corn promised to be a favorable subject as the leaves are thin and assimilate strongly. This plant contains large amounts of pentosans, 17 per cent. in the leaves and 11.5 in the stems. The first investigation showed that one square meter of leaves weighed in the evening 33.456 grams and in the morning 28.633 grams. During the night 4.823 grams were removed and still one square meter of leaves contained in the morning ninety-eight mgms. more pentosans than in the evening. As it seemed possible that a small amount of pentosan was formed during the night in the leaves I collected in my second investigation first in the morning and afterwards in the evening, I found that one square meter of leaves had stored during the day 3.710 grams of dry matter, but no pentosans, since eighteen mgms. more were found in the morning, which difference is well within the limits of experimental error. Oak leaves had also to be investigated, as little difference was found in the amount of soluble pentosans in morning and evening leaves. They offer a much less favorable subject than corn leaves, since they are thicker and do not assimilate as strongly. Oak plants are, however, also rich in pentosans. The leaves, it is true, contain only from seven to eight per cent., but the stems, which weigh far more, are also much richer in these substances. The stems of the shrubs which I used contained nineteen per cent. of pentosan.

In the experiments made I collected first in the evening and afterwards in the morning. The plants used for the two experiments belonged to two different localities. The results of both investigations showed slightly more pentosans in the morning, but the differences found do not exceed the limits of experimental error. The seeds of *tropaeolum majus* contain a pentosan that is soluble in boiling water and conducts itself also in other respects as starch. I therefore experimented also with this plant. The plants contain but little pentosan, the leaves 4 per cent., and the stems 6.5. The leaves are very thin, and therefore I was obliged to take 300 leaves in order to obtain enough substance for the estimation of the pentosans. These leaves were cut during several evenings and nights in succession. One square meter of leaves lost during the night 2.742 grams of dry matter, but only fourteen mgms. of pentosan.

All these investigations show that an accumulation of pentosans in the day time and transportation of the same during the night does not take place. The pentosans therefore are not formed by the assimilation process, unless in such imperceptible quantities as can not explain the large amounts that plants contain.

The theory of Fischer, according to which a formation of pentoses by the assimilation process is improbable, thus receives unexpected support.

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## IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

BY PETER S. GILCHRIST.

Received September 11, 1893.

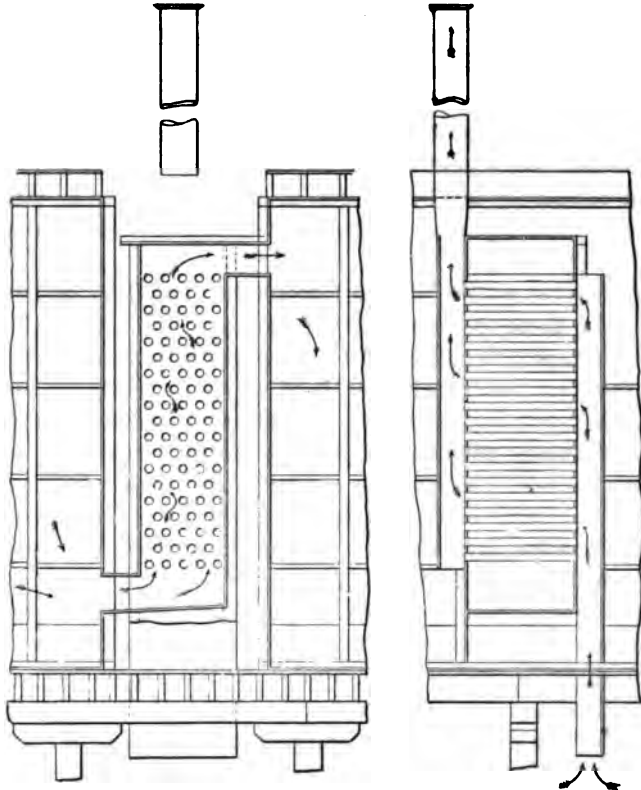
ANYTHING tending towards cheapening the cost of producing sulphuric acid has now become of vital importance to chemical manufacturers. The chief source of improvement lies in the reduction of the large chamber space necessary for condensation, owing to its cost and maintenance. This has been attained in several ways.

A simple but very effective method has been devised by Hacker and Gilchrist, which has been attended with very satis-

factory results, their device having been covered by patents in this country and in England.

**DEVICE FOR SAVING CHAMBER SPACE.**

Hacker & Gilchrist's Patent.



The gases in passing from one chamber to another, are drawn through a leaden tower, called a pipe column. This column is filled with horizontal lead pipes burnt to the sides, and so placed as to continually break the course of the gases, but at the same time allow them to pass.

Through the horizontal pipes, air of ordinary temperature is drawn, by means of a chimney, or preferably by artificially cold air forced through by means of an air pump.

During the passage of the gases through these columns they



are thoroughly mixed, a strong reaction resulting, consequently heat is evolved. This heat is carried off by means of the cold air passing through the pipes. Moisture is supplied by steam entering into the column along with the gases, or by running weak acid down the column.

These towers or pipe columns can be placed between the Glover and the first chamber, between the several chambers, and between the last chamber and Gay-Lussac towers. The object of this last position is to cool the gases, and remove the last traces of sulphuric acid before entering the Gay-Lussac tower, so that it can be used fully for absorption, for in so many instances the lower part of the tower is simply lost for the recovery of the nitrous gases.

At the works of the Wando Phosphate Company, of Charleston, S. C., these columns have been adopted. The chamber capacity is 246,400 cubic feet. The plant consists of four chambers, the first three being each of 78,400 cubic feet capacity, and the last one 11,200 cubic feet capacity, with Glover, and two Gay-Lussac towers. There are thirty-eight lump pyrites burners, each of 750 pounds capacity per twenty-four hours of fifty-two per cent. ore, making the chamber space for sulphur actually burnt a little under seventeen cubic feet per one pound of sulphur, per twenty-four hours.

There can be readily added six additional furnaces to thirty-eight, increasing them to forty-four, as chambers three and four are simply storages for nitre, almost all the acid being made in the first and second chambers. This would bring the capacity down to fifteen cubic feet per one pound of sulphur burnt.

The yield of acid has been in the neighborhood of 4.75 pounds of 50° B. acid per one pound of sulphur. As the pipe columns were added to a plant already built, they could not be placed to the best advantage; the first three chambers being 160 feet long, the pipe columns are at too great a distance from each other, so are not as effective as if in conjunction with smaller chambers.

These pipe columns need little attention, as the steam being regulated by the strength of the drip, when once regulated need not be touched, if the steam for the chambers is supplied through a self-regulating pressure gauge.

The advantage of the pipe columns in warm climates is very great, the yield of acid per chamber space being largely increased, thirty to forty-five per cent., according to the number of pipe columns used. The yield of acid per quota of sulphur is also increased, and a saving of nitre is effected. These towers being made of lead, are not very expensive, so are likely to become adjuncts to many chambers, especially as they can be added to existing plants.

Since this paper was written, I have planned two new acid plants, saving chamber space by means of the foregoing device; these two plants are now under course of construction.

CHARLESTON, S. C.

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### THE EDUCATION OF INDUSTRIAL CHEMISTS.<sup>1</sup>

BY HENRY PEMBERTON, JR.

SOME years ago a chemical firm in one of our eastern cities was desirous of obtaining the services of a chemist, who should take charge of the factory. Accordingly, advertisements were inserted in the industrial journals, for a man who should not only be familiar with the analytical work necessary, but who could also assume the responsibility of overseeing the plant, checking the running of the various processes, and meeting the emergencies that are constantly arising in operations of this kind.

A large number of answers were received. Interviews were requested with those who, from their letters, appeared to be the most likely to suit. But as a result, it soon appeared that the securing of a competent man was by no means an easy matter. Some of the applicants, whose letters were most assuring, turned out to have been simply laboratory boys. Others, more promising, were of foreign birth, but unfamiliar with the language and customs of this country. Some were undesirable on account of their personal manner or character. But, by far the most general objection, was that the knowledge and experience of these chemists were limited to the field of analytical chemistry, and to the work of the laboratory. They were entirely familiar with the handling of beaker glasses and funnels, plati-

<sup>1</sup> Read before the Worlds' Congress of Chemists, August 26, 1893.

num crucibles, analytical balances, burettes, and flasks. But in the matter of treating material *in large quantities*, and obtaining results in the factory, they came up, as it were, against a stone wall. Many of them, in fact, were literally as unfamiliar with the operations of a chemical plant as they were with the working of an astronomical observatory.

It should be observed that the case here described, is by no means an isolated one. There is reason to believe that there is hardly a large chemical manufacturer in the country who, at one time or other in his life, has not had experiences of a nature similar to this one.

It will be admitted that the question of technical education is a most important one. It deserves at least as much attention in the United States as it does elsewhere, on account of the remarkable progress and development of industrial activity here. It will be shown in the forthcoming report of the United States Census of Manufactures, that the chemical industry has experienced a more diversified and extended growth than is peculiar to any other branch of productive industry in this country. Owing to the richness of our resources (which we have always enjoyed), and owing especially to the beneficent effects of a high tariff (which we have enjoyed for three decades) the capital invested, the wages paid, and the value of the chemicals and allied products manufactured, represent in the aggregate a degree of prosperity that is most flattering.

It is for this important field then, that the universities and technological schools of the country, prepare their young men. And it is because the quality of this technical talent is so frequently below what is called for, that I venture to draw attention to certain considerations on the subject, that may be of interest.

The method of teaching applied chemistry as now generally practiced consists in describing, in a series of lectures, the manufacture of so many of the various acids, bases, and salts as the professor can find time to present. Sometimes certain industry groups are selected, such as soda chemicals, explosives, dye extracts, coal tar products, and so on. But it is evident, on account of the endless array of chemical products, that it is

impossible to cover the ground in any but the most superficial manner. It is also an even chance whether the student will ever afterwards be engaged in any of the few industries thus outlined by him in his lecture note book.

It should again be stated that the usual method of instruction consists in describing the manufacture of certain *products*: the preparation of this salt, of that acid, or of that dye. It is invariably upon a series of such products that the classification of the lectures is based, and it is because the name of these chemicals is legion that the instruction must necessarily be incomplete and the knowledge gained vague and indefinite. While such instruction is, of course, better than none, and indeed should still be continued, it should be relegated to the position in the curriculum to which it properly belongs, as being a part of the course in general chemistry adapted to all chemical students, but should not be the only groundwork for the training of the future technologist.

What is it that such a young man sees on entering one of our large chemical factories? He observes, on all sides of him, apparatus and machinery for grinding material, for elevating and transporting it. He sees materials under treatment in various ways, and at all stages. He notices that in one building or department such and such operations are performed—it may be the solution of some article here, the filtration and washing there. Here he sees the processes of evaporation, or it may be of crystallization or perhaps of distillation and condensation. Elsewhere he observes a series of calcining furnaces. In another part of the works are the drying rooms. Many other processes he notices in full operation, the object of which, and perhaps of the very name of which, he is ignorant. The thought that is likely to be deeply impressed upon his mind is—"Why was I taught nothing of this in college?" His mortification is apt to be all the greater when he perceives the number of workmen about him who understand it all. There are foremen, heads of departments, machinists, carpenters, and others, no one of whom, perhaps can write a letter correctly, and yet all experts in their several lines; while he, a university graduate, has not even been taught the use of the tools of his trade.

It is evident that some system of instruction is necessary that is essentially different from that now in vogue. And it is the object of this paper to outline such a plan, which, it may be stated at once, *consists in the teaching, not of products, but of processes, and in directing the attention not so much to the chemical, as to the apparatus.* The subject can be discussed most clearly by presenting it under three headings: The lectures, the practical work, and the text book.

*The Lectures.*—Prof. Tyndall once observed that a man who had thoroughly mastered a scientific principle was in possession of a key that would open many locks. A somewhat similar idea is here applicable; the important point being to place the learner in possession of the knowledge of one particular class of operations at a time, and to make that knowledge comprehensible and thorough, so that its application to any variety of purposes may be possible.

For example, let a series of lectures be given upon the reduction of materials to a fine state of division. The many kinds of crushers, chasers, mills, disintegrators, and beaters should be described, especial attention being given to explaining the peculiar adaptability of each kind of such machinery to the physical properties of the substances to be treated. A thorough description of the practical working points of each type of mill should be laid before the student. In the case of an ordinary pair of forty-eight inch buhrstones for example, he would be taught such facts as the average horse power required to drive them, the usual output of the mill per hour, the speed at which it runs, the dress of the stones, and the different qualities of materials from which they are made. The use of screens and bolting cloths would be touched upon, as well as the methods of handling the tailings. Some mills he would observe are capable of yielding a product large in quantity, but coarse in quality, while others can be used only under conditions exactly the reverse. Some forms of apparatus like the disintegrator, can treat a damp or plastic material, such as a superphosphate or sulphate of alumina, while others will handle dry and brittle substances, only, to advantage.

An understanding of the essential principle upon which each

of these forms of apparatus works would thus be obtained by the student, who would be able to apply the information, it may be years afterwards, in some distant fertilizing factory in Georgia, or in some remote refining works in the far West.

Continuing the same line of thought another series of lectures would be given upon filtration, frequently one of the most difficult of technical processes. It could be shown how a coarse open substance (like black ash for instance) can be washed in masses of considerable depth, while others, of a closer or denser nature, like lime-mud, or calcium sulphate, must be handled in what, to the tyro, would appear to be amazingly thin and extended surfaces. It would be pointed out how some substances, like gelatinous hydrate of alumina or precipitated ferric hydrate, cannot be filtered at all, practically, on a large scale, but must be washed by decantation. The construction of filters, the selection of proper materials for the filter bed, the application of a vacuum, the handling of the different wash waters, the use of filter presses, and of centrifugals, all of these matters would be discussed in sequence. This would form a scientific classification of the subject that would be valuable to the student, enabling him to apply the information to the preparation of any kind of chemicals, let them be fine pharmaceutical preparations, or heavy bulky goods that are made in large quantities.

The methods of evaporation of liquids could next be studied, describing the plant necessary for underheating, for surface heating, and for coil evaporation. The treatment of solutions with gases, the methods of uniformly mixing solids with liquids, the erection and use of reverberatory furnaces, the transportation of solids by elevators, conveyors, belts or link chains, the lifting of liquids, acid or alkaline, by pumps, injectors, or compressed air; in a word, all the important processes in use in chemical engineering would each, in turn, form the subject of a series of lectures.

In teaching applied chemistry in this manner the important point gained is that the learner's mind is occupied by one class of subjects, or processes at a time, thus giving him a practical knowledge of each important department of manufacturing

chemistry, *entirely irrespective of what kind of goods are produced*. This is in sharp contrast to the present systems, in which his mind is bewildered by the numerous details involved in the description of a heterogeneous series of chemicals. He perceives that the forms of apparatus in use in the factory are simply so many tools, the construction and use of which he must learn in order to obtain results, and that when equipped therewith he is "in possession of a key that will open many locks."

*The Practical Work.*—The study of analytical chemistry, although an excellent training for the mind, has one element of weakness: the learner is taught to depend entirely upon authority. He is obliged to follow out, to the very letter, the methods prescribed in the text book. As a result, he necessarily foregoes any attempt at original work, and as a specialist in analytical chemistry is frequently (in fact almost always), incapable of supervising any work other than that of the laboratory.

The remedy for this is to catch the chemist when he is young, and introduce him to the methods used on the large scale. It is seldom possible to obtain for a student the entrée to a chemical works. Such a request is generally declined without thanks. And as the chemical works cannot be brought into the college, it remains that there be established there certain methods of work requiring the same processes of reasoning and the same methods of attacking the problems that are in use in the actual factory.

The important facts so far as *apparatus* is concerned, can be obtained from the lectures, and still more fully from the text book. But in regard to the methods of working, valuable information can be had from synthetic experiments of the simplest nature. And it is in such investigations that the student should be well drilled. As an example of the points that can be illustrated in this manner, let a student be required to make, for instance, some copperas, for which purpose he may be furnished with a few ounces of iron nails, some oil of vitriol, a number of large dishes and a funnel. He determines the strength of the acid, using both Twaddle's and Beaumé's hydrometers, thus

learning the use of these instruments. Converting this into specific gravity he obtains from the tables the percentage of actual  $\text{SO}_2$  in the acid, and from that the volume of vitriol required for the given weight of iron. He next calculates the quantity of water necessary to supply the water of crystallization of the salt, as well as that required to hold it in solution, and by this means becomes familiar with the use of tables of solubilities. After solution of the iron and filtration, he measures the total bulk of the liquid, which is then evaporated to the crystallizing point, and again measured. The conditions most favorable to crystallization are now studied, the weight of crystals obtained and the percentage yield as compared with that of theory, computed. Analysis of the mother liquor will check this, and will familiarize him with the method of calculating milligrams per cubic centimeter into pounds per cubic foot.

He is now in position to estimate the size of the vessels necessary to treat a batch of say 1,000 pounds of iron, and can, on paper, erect a dissolving tub, filter, evaporating tank, and crystallizer, all of the proper shape and proportion. The best thickness of lead for lining these tanks can be determined, its weight calculated and also its cost. Assuming a price for the iron and vitriol, the cost of these ingredients per ton of crystal can easily be figured out. And all of this from a bottle of acid and a few ounces of iron nails.

This little example is given merely as an illustration of what kind of work can be done. It can of course be varied in many ways and with many materials. It matters not a particle upon what salt or preparation the student is put to work. As a matter of fact the above example would never be put into practice on the large scale, since copperas is nearly always produced as a by-product from other operations, or is made by the weathering of marcasite.

But the training that he obtains will teach him the importance of observing the physical properties of substances in the various stages of treatment. By discovering the difficulties to be met he acquires the art of *making mistakes on the small scale*. The lack of such experience has undoubtedly been the cause of the loss of immense sums of money in many instances.



*The Text Book.*—To this entire subject of industrial education, as herein described, there is one objection that may be made, namely: What is to prevent such a series of lectures becoming antiquated and out of date in the course of a few years? The answer is to be found in the literature of the subject. How many text books on qualitative analysis are there in existence? As every chemist knows, they are numbered by the score, if not by the hundred. In what important particular does any one of these text books differ from the others? What new fact does it contain? If, now, a subject so utterly thrashed out as qualitative chemical analysis can thus be again and again discussed, what is to prevent the establishment of a series of treatises on chemical technology, by which the whole subject can be brought under control and properly classified? It is important to note that such treatment of the subject would of necessity be *cumulative*. The experience of one writer would thus be collected and embodied in the treatise of another. The weak points of one text book would be made good in its successor, or in the second edition. The mere fact that no such treatises are in use to-day is precisely the most imperative reason why they should be introduced.

Such a manual would follow the methods indicated in the foregoing. Its object would be to describe not products, but processes, and it would be to the apparatus and methods of treatment that attention would be given. It is needless again to go over the ground previously covered, more than to say that each particular class of operations in use in a factory would be treated separately in its proper chapter. In other words, the book would supplement the lectures. The illustrations and plans to scale would describe actual working apparatus and the student would be taught how to handle precipitates and solutions by the ton, just as, in analytical work, he learns to manipulate them in quantities represented by the gram and cubic centimeter.

In addition to such a treatise, the student should be allowed the use of the various journals on chemical technology that are published in the English and German languages. To these should be added the trade journals, of which there are quite a

number, and even such material as manufacturer's catalogues and illustrated price lists will be found to contain information of much value upon subjects relating to the supplies needed in all factories.

In conclusion it may be acknowledged that this plan of instruction is essentially a utilitarian one. This is in accordance with the general drift of the scientific education of to-day. To use Lord Bacon's expression the aim is to gather fruit, not flowers. The training of the mind will incidentally be one of the results of such a system. But the main object will be the imparting of actual knowledge and the teaching of specific facts. The manufacturing chemist who has to meet the difficulties that constantly arise in the practice of his profession is like a man who is lost in the Alps. What he wants, is not to improve his mind, but to find the way. The present system of instruction does not meet the requirements made upon it. It teaches the principles of the science but does not go far enough. As Macaulay said of the ancient philosophers, every trace of intellectual cultivation is there except a harvest. The subject of industrial chemistry evidently has not received the attention it deserves in our schools of science.

PHILADELPHIA, PA.

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#### THE DETERMINATION OF CASEIN IN COWS' MILK.

BY L. L. VAN SLYKE.

Received August 31, 1893.

THE methods originally proposed by Hoppe-Seyler and Ritthausen have been commonly employed for the separation and determination of casein in cow's milk. In both methods, the milk is diluted with water and a small amount of acetic acid is added. The precipitation is rendered complete, in one case, by raising the temperature to 40° C., and, in the other case, by passing a current of carbon dioxide through the mixture at ordinary temperatures. The precipitate is filtered, washed first with water, and then with ether to remove fat and is finally dried and weighed on the filter. The absence of specific directions touching several steps of the operation led me to investigate some of the conditions pertaining to the determination of casein, among which were the following:

1. Comparison of the two methods.
2. Influence of amount of acid used in precipitating casein.
3. Use of different acids in precipitating casein.
4. Influence of temperature and time of digestion on precipitation of casein.
5. The precipitation of casein in fresh and in old milk.
6. The use of preservatives in keeping milk, and influence on the determination of casein.

The tedious method involved in washing the precipitated casein free from fat by ether and in subsequent drying and weighing on the filter paper was entirely discarded. The precipitated casein was washed by decantation and on the filter two or three times. The filter and contents were then treated by the ordinary Kjeldahl method for the determination of nitrogen, the factor 6.25 being used to convert the amount of nitrogen into an equivalent of casein, when this was desired. This use of the Kjeldahl method in determining the amount of casein was suggested and employed sometime since by several chemists and is now very generally used in the analysis of dairy-products. The advantages of its use over the old method in point of accuracy and simplicity are too evident and too well known to deserve further mention. Much credit is due to Mr. A. L. Knisely who has done valuable work in carrying out the analytical details of the investigation.

(1) *Comparison of Results Obtained by Precipitating Casein in Milk at a Temperature of 40° C. without Carbon Dioxide and with Carbon Dioxide at Ordinary Temperatures.*—The method employed in making the comparison was, briefly, as follows: About ten grams of milk were used in each case. This amount of milk was diluted with water at 40°–42° C. to 100 cc. and then 1.5 cc. of a solution containing ten per cent. of acetic acid were added and the solution was carefully stirred with a glass rod. The resulting precipitate was washed two or three times by decantation and on the filter; finally, the filter-paper and contents were digested according to the Kjeldahl method for determining nitrogen. In the other case, the milk was diluted to 100 cc. with water of the temperature of the room, then 1.5 cc. of the same dilute acetic acid as that employed above were added,

after which a stream of carbon dioxide was passed through the solution, until the liquid above the precipitate was clear or very nearly so. The subsequent filtration, washing, and determination of nitrogen were made as above.

The following results were obtained by the two methods with two different samples of milk, triplicate determinations being made in each case :

Method A, precipitation at 40° C., sample No. 1.				Method B, precipitation with aid of carbon dioxide, sample No. 1.			
(a)	0.475	....	per cent. nitrogen	(a)	0.486	....	per cent. nitrogen
(b)	0.474	....	" " " "	(b)	0.480	....	" " " "
(c)	0.469	....	" " " "	(c)	0.461	....	" " " "
Average 0.473				Average 0.476			
Sample No. 2.				Sample No. 2.			
(a)	0.458	....	per cent. nitrogen	(a)	0.454	....	per cent. nitrogen
(b)	0.458	....	" " " "	(b)	0.444	....	" " " "
(c)	0.449	....	" " " "	(c)	0.455	....	" " " "
Average 0.455				Average 0.451			

*Statement of Results.*—The above results indicate: First, that essentially the same results are obtained whether we precipitate the casein in cows' milk at a temperature of 40° C. without carbon dioxide, or at ordinary temperatures with the aid of carbon dioxide, other conditions being uniform. In sample No. 1, the results differed by 0.003 per cent. of nitrogen; in sample No. 2, by 0.004 per cent. of nitrogen, the excess being first with one method and then with the other.

Second, that the individual results obtained by several determinations of the same milk agree closely by either method, somewhat closer concordance being given by precipitation at 40° C. Thus, in sample No. 1, the greatest difference in three determinations was 0.006 per cent. of nitrogen at 40° C., and 0.025 per cent. nitrogen with the other method. In sample No. 2, the greatest difference was 0.009 per cent. nitrogen at 40° C. in three determinations, and 0.011 per cent. nitrogen with the other method.

(2) *Influence of Amount of Acid Used in Precipitating Casein.*—The acid used was a solution containing ten per cent. by weight of acetic acid. This dilute acetic acid was used in amounts

varying from 0.5 to 5 cc. To about ten grams of milk, sufficient water at 40°-42° C. was added to dilute to 100 cc. and the acetic acid was then added. The operation was completed in the manner described above.

Below we present the analytical results tabulated:

	Amount of acid used.	Character of filtrate.	Per cent. of nitrogen found in the precipitate.
Sample No. 1.....	0.5 cc.	slightly cloudy .....	0.458
	1.0 "	clear .....	0.458
	2.0 "	clear .....	0.449
	3.0 "	clear .....	0.441
Sample No. 2.....	1.0 cc.	clear .....	0.475
	1.5 "	clear .....	0.474
	2.0 "	clear .....	0.469
	3.0 "	slightly cloudy .....	0.450
Sample No. 3.....	0.5 cc.	milky .....	0.117
	1.0 "	quite cloudy .....	0.471
	1.5 "	clear .....	0.545
	2.0 "	clear .....	0.550
	2.5 "	clear .....	0.545
	3.0 "	clear .....	0.537
	4.0 "	slightly cloudy .....	0.527
Sample No. 4.....	5.0 "	milky .....	0.340
	0.5 cc.	milky .....	0.059
	1.0 "	slightly cloudy .....	0.551
	1.5 "	clear .....	0.550

*Statement of Results.*—The data presented in the preceding table indicate:

First, that in one sample 0.5 cc. of acid gave a maximum amount of nitrogen in the precipitate, while in two other samples, the amount of nitrogen obtained in the precipitate was very low. In each instance where the lowest results were given, the filtrate was milky in appearance.

Second, that in three samples out of four, the use of 1.0 cc. of acid gave highest results, the filtrate being clear or only faintly cloudy.

Third, that, in most instances, the use of 1.5 cc. of acid gave the highest results, with a clear filtrate in every case.

Fourth, that the use of two cc. of acid gave very nearly the same results as the use of 1.5 cc. of acid in most cases, the filtrate being clear.

Fifth, that the use of 2.5 cc. or more of acid gave lower results, the decrease becoming greater with increase of acid and the character of the filtrate becoming more turbid in appearance.

Sixth, that, with fresh milk, the best results can be secured in determining casein by using from one to two cc. or, in general, 1.5 cc. of a ten per cent. solution of acetic acid.

Seventh, that the completeness of precipitation is quite fairly indicated by the character of the filtrate. When the precipitation is incomplete as a result of using too little acid, the filtrate will be more or less turbid, varying from opaque milkiness to barely perceptible cloudiness. If, on the other hand, an excess of acid is used, thereby causing more or less casein to remain in solution, the filtrate will be more or less turbid according to the amount of casein in solution. In some cases, a filter paper may allow some precipitated casein to pass through and render the filtrate turbid. In such cases, two or three repeated filtrations generally serve to remove the casein and to give a clear filtrate.

(3) *The Use of Different Acids in Precipitating Casein.*—In order to ascertain whether some other acid could be used to precipitate casein more effectively than acetic acid, comparative trials were made with solutions containing ten per cent. of the following acids: (1) acetic, (2) lactic, (3) sulphuric, (4) hydrochloric. Below are given the results of the comparative trials:

Kind of acid used.	Amount of acid used.	Character of filtrate.	Character of precipitate.	Per cent. of nitrogen in precipitate.
Acetic acid	1.5 cc.	clear	flocculent	0.395
Lactic acid	0.5 "	milky	"	0.074
" "	0.75 "	slightly cloudy	"	0.396
" "	1.0 "	clear	"	0.394
" "	1.5 "	milky	"	0.268
Acetic acid	1.5 cc.	clear	flocculent	0.465
Sulphuric acid	0.5 "	clear	s'ewh't gelatinous	0.470
" "	0.75 "	clear	" "	0.457
" "	1.0 "	cloudy	" "	0.417
Acetic acid	1.5 cc.	clear	flocculent	0.464
Hydrochloric acid	0.3 "	cloudy	gelatinous	0.410
" "	0.5 "	cloudy	"	0.404
" "	0.75 "	milky	"	0.199

*Statement of Results.*—The results contained in the foregoing table show :

First, that lactic acid gives results closely agreeing with those obtained by the use of acetic acid, when about one cc. of a ten

per cent. solution of lactic acid is used, but if 0.5 cc. more or less than one cc. of lactic acid are used, the results are very low. The precipitate was flocculent and filtered readily.

Second, that a ten per cent. solution of sulphuric acid when used to the extent of 0.5 cc. for ten grams of milk gave results closely agreeing with those given by the use of acetic acid, but that when more than 0.5 cc. were used, the results became lower. The filtrate was clear, but the casein did not separate in flocculent condition, having a tendency to become gelatinous. Several filtrations were required to get a clear filtrate, and filtration was slow.

Third, that very unsatisfactory results were given by the use of hydrochloric acid, whatever the amount used. The filtrate was cloudy or milky, the precipitate gelatinous, the filtration extremely slow, and the results low.

Fourth, for the most satisfactory results, for the flocculent character of the precipitate, for rapidity of precipitation, filtration, etc., the use of acetic acid had a great advantage over the other acids tried.

(4) *Influence of Temperature and Time of Digestion on Precipitation of Casein.*—In making the experiments, the results of which are tabulated below, the temperature and time of digestion were made to vary, all the other conditions being kept uniform.

Temperature of digestion.	Time of digestion.	Character of filtrate.	Per cent. of nitrogen in precipitate.
30° C.	5 minutes	clear	0.448
40° "	0 "	"	0.475
40° "	1 "	"	0.479
40° "	2 "	"	0.481
40° "	3 "	"	0.471
40° "	10 "	"	0.477
40° "	20 "	"	0.484
45° "	0 "	"	0.468
45° "	2 "	"	0.476
45° "	5 "	"	0.483

The data presented in the foregoing table show:

First, that, when the precipitate was digested at 30° C. for five minutes, the results were lowest.

Second, that, when the precipitate was digested at 40° C.

without standing or with standing one, two, three, ten, or twenty minutes, the results were practically uniform. The greatest difference obtained by digesting different periods of time did not exceed 0.01 per cent. nitrogen.

Third, that, when the precipitate was digested at 45° C. for periods of time varying from a few seconds to five minutes, the results were fairly uniform, the greatest difference being 0.015 per cent. nitrogen. As compared with digestion at 40° C., digestion at 45° C. gave essentially the same results.

Fourth, it would, therefore, seem that a variation of temperature two or three degrees above or below 40° C. and variation of time of digestion after the addition of acetic acid exercises comparatively little influence upon the results. However, in practice, I think it is desirable to adhere quite closely to uniformity of temperature.

(5) *The Precipitation of Casein in Fresh and in Old Milk.*—The fact is well known that milk undergoes rapid and complex changes when left to itself at ordinary temperatures. In the course of our work, it occurred to the writer that, as a result of these changes, the casein might be so changed that the method used in determining casein in fresh milk might not be entirely applicable to milk that had undergone more or less change; or that the formation of lactic acid might make necessary the use of less acetic acid than is used in precipitating the casein of fresh milk. It was generally found that, after milk had stood at a temperature of 17° to 22° C. for twenty-four hours or more, the use of 1.5 cc. of a ten per cent. solution of acetic acid gave low results, the filtrate being decidedly turbid. In some cases the casein was almost entirely rendered soluble and passed into the filtrate. It was found that the only method of handling milk under such circumstances was to add the acetic acid to the milk, diluted with water at 40°-42° C., in small portions of a few drops at a time, stirring after each addition and continuing the additions until the liquid above the precipitate became clear or nearly so. But, even with this treatment, there was found to be more or less loss. The terms "fresh" and "old" milk are, of necessity, rather vague. Much depends upon the conditions under which milk is kept. The extent of



change rather than the actual age of the milk should form the basis of distinction. Coagulated milk gave low results.

	Age of milk.	Per cent. of nitrogen in precipitate.	Amount of loss.
Sample No. 1.....	Fresh.....	0.429	....
	7 days.....	0.378	0.051
Sample No. 2.....	Fresh.....	0.447	....
	1 day.....	0.427	0.020
	3 days.....	0.428	0.019
	7 days.....	0.428	0.019
Sample No. 3.....	Fresh.....	0.428	....
	1 day.....	0.410	0.018
Sample No. 4.....	Fresh.....	0.438	....
	1 day.....	0.415	0.023
Sample No. 5.....	Fresh.....	0.624	....
	1 day.....	0.617	0.007
Sample No. 6.....	Fresh.....	0.397	....
	1 day.....	0.397	0.000
Sample No. 7.....	Fresh.....	0.466	....
	1 day.....	0.445	0.021

The author has in progress an investigation relating to the detailed changes that take place in the nitrogen compounds of milk under various conditions.

*Statement of Results.*—First, when milk was kept at a temperature of 17° to 22° C. for twenty-four hours, the amount of nitrogen as casein was found, in most cases, to be nearly 0.02 per cent. less than in fresh milk.

Second, in case of one milk kept seven days, the amount of nitrogen in the casein was 0.051 per cent. less than in fresh milk, while, in another case, it was 0.019 per cent. less.

Third, in general, it was found necessary, in order to get results that were at all satisfactory, to use less than 1.5 cc. of dilute acetic acid to precipitate the casein in milk that had been standing long enough to undergo any marked change.

Fourth, while good results may, in exceptional cases, be secured in determining casein in milk that has undergone noticeable change without any modification of the method given for the determination of casein in fresh milk, the accuracy of such determinations must be regarded as uncertain in regular work.

(6) *The Influence of Mercuric Chloride Used as a Preservative on the Determination of Casein in Milk.*—In view of what has

just preceded, can we be certain of our results when we determine casein in milk that is not fresh? The thought suggested itself to the author that if some germicide could be added to fresh milk to prevent or retard the changes that affect the casein, then we might be able to determine the casein in milk that had stood indefinitely. In order to test the question, finely powdered mercuric chloride was used in proportion of about one part of mercuric chloride to two thousand parts of milk by weight. A sample of milk was analyzed when fresh and portions were set aside for varying periods of time, some with and some without the addition of mercuric chloride. Determinations of casein were made from time to time, using less than 1.5 cc. dilute acetic acid. The results were as follows:

Age of milk.	Per cent. of nitrogen in precipitate when no	Amount of loss.	Per cent. of nitrogen in precipitate when	Amount of loss.
	mercuric chloride was used.		mercuric chloride was used.	
Fresh .....	0.447	...	0.447	....
1 day .....	0.427	0.20	0.444	0.003
3 days .....	0.428	0.19	0.444	0.003

*Statement of Results.*—The foregoing results appear to indicate :

First, that the use of mercuric chloride in fresh milk largely prevents or retards the occurrence of those changes that effect the determination of casein.

Second, that even when mercuric chloride is used in milk, it is generally desirable to use less than 1.5 cc. of dilute acetic acid in precipitating the casein.

Third, that the use of mercuric chloride in the proportions stated did not precipitate in appreciable quantity any nitrogen compounds such as albumen.

(7) *General Summary.*—We may summarize the results of our work as follows :

First, precipitation of casein in cows' milk gives essentially the same results whether made at 40° C. without carbon dioxide or at ordinary temperatures with the aid of carbon dioxide, other conditions being uniform.

Second, between one and two cc. of a ten per cent. solution of acetic acid, generally about 1.5 cc., gave the best results.

Third, the use of lactic acid, sulphuric acid, and hydrochloric

acid gave results much less satisfactory than the use of acetic acid.

Fourth, a variation of a few degrees from 40° C. and a variation of time of digestion after the addition of acetic acid exercised comparatively little influence on the results.

Fifth, the precipitation of casein in milk that had undergone noticeable change was generally found to give lower results than in case of the same milk when fresh, even when less than 1.5 cc. of acetic acid were used. Coagulated milk always gave low results compared with fresh milk.

Sixth, the use of mercuric chloride in fresh milk, in the proportion of one part of the former to two thousand parts of milk, largely prevented or retarded the occurrence of those changes that affect the determination of casein in old milk.

Seventh, in a general way, the character of the filtrate serves as a fairly reliable guide in regard to the completeness of the precipitation of casein from milk. When the filtrate is clear or only perceptibly cloudy, the precipitation is generally complete; but, when the filtrate is decidedly turbid or milky and two or three repeated filtrations do not remove the turbidity, the precipitation will generally be found incomplete and such a determination, if carried out, will give low results.

(8) *Detailed Description of Method Used in Determining the Casein of Cows' Milk.*—I. In Fresh Milk: Weigh out about ten grams of milk, dilute in a beaker with about ninety cc. of water at 40°–42° C., and add at once 1.5 cc. of a solution containing ten per cent. of acetic acid by weight. Stir with a glass rod and let stand three to five minutes or longer. Then decant on filter, wash two or three times with cold water by decantation, and then transfer precipitate completely to filter. Wash once or twice on filter. The filtrate should be clear or very nearly so. If the filtrate is not clear when it first runs through, it can generally be made so by two or three repeated filtrations, after which the washing of the precipitate can be completed. The washed precipitate and filter paper are then digested as in the regular Kjeldahl method for the determination of nitrogen and the determination of nitrogen is completed as usual. To calculate the nitrogen into an equivalent amount of casein, multiply the

amount of nitrogen found by the factor 6.25. Ordinarily, for this purpose, milk can be regarded as "fresh," when it does not show marked development of lactic acid.

II. In Old Milk: When milk has undergone such change as to show marked development of lactic acid, the method above given cannot generally be relied upon to give accurate results in determining casein. So far as our results go, they indicate that we cannot with positive accuracy determine casein in such milk by any method now known, and results obtained with changed milk must be regarded as only approximate. If, however, one part of finely powdered mercuric chloride is added to two thousand parts of milk, when fresh, the changes, which would otherwise take place, are prevented or greatly retarded, so that milk treated in this manner may be used after standing some days for the determination of its casein. In such cases, the method given above for fresh milk may be followed, except that the acetic acid should be added in small portions, a few drops at a time, stirring after each addition, and continuing the addition of acetic acid until the liquid above the precipitate becomes clear or very nearly so.

NEW YORK STATE AGRICULTURAL EXPERIMENT  
STATION, GENEVA, N. Y.,  
AUGUST, 1893.

### SOME POINTS RELATING TO THE COMPOSITION OF COWS' MILK.<sup>1</sup>

BY L. L. VAN SLYKE, CHEMIST OF N. Y. AGR. EXP. STA.

IT is my purpose to call attention to some general results secured in our work at the New York State Agricultural Experiment Station at Geneva in the course of an extended examination of the milk of cows in that State. Our results are based upon the analysis of lots of milk aggregating over 200,000 pounds and representing the product of not less than 1,500 individual animals, and 20,000 separate milkings extending over a period of some six months.

The points to which I wish to call especial attention are the following:

1. The relation of casein to albumen in normal milk.

<sup>1</sup> Read before the World's Congress of Chemists, August 24, 1893.

2. The relation of fat to casein and albumen in normal milk.
3. The relation of fat to casein (excluding albumen) in normal milk.
4. The effect of removing fat from normal milk upon the relation of fat to casein.
5. The relation of fat to total solids in milk as defined by law.

(1) *The Relation of Casein to Albumen in Normal Milk.*—In the present state of our lack of detailed knowledge regarding the constitution and relations of the nitrogen compounds of milk, we call casein that portion of the nitrogen compounds of milk that is precipitated by rennet, dilute acids, and certain salts. The remaining portion of the nitrogen compounds of milk we call albumen, though we know that there are at least two different compounds in this portion. The casein was determined by precipitation with dilute acetic acid and the nitrogen in the precipitate estimated by the regular Kjeldahl method, the nitrogen multiplied by 6.25 gave casein. The details of the method are contained in a paper presented elsewhere by me. The amount of casein subtracted from the total amount of nitrogen compounds in the milk gave the albumen by difference.

The point to which I wish to direct attention in this connection is this: Do casein and albumen in the normal milk of cows bear a definite or a variable relation to each other? So far as I have been able to ascertain, the only positive statement on this point has been made by Blyth (*Foods: Composition and Analysis* 2. ed., p. 208,) and he says: "The amount of albumen in milk is really fairly constant, and averages 0.7 per cent. In healthy cows it is a very constant quantity, the chief deviation occurring directly after calving, when the amount may rise as high as three per cent., but this is always accompanied by a corresponding rise in the casein. According to the author's experience, the albumen preserves a very constant relation to the casein, the quantity of the latter being five times that of the albumen; so that if either the amount of casein or albumen is known, the one may be calculated from the other with great accuracy." The foregoing statement has been quite generally accepted as authoritative. It is to be regretted that Blyth does not state the extent of the work upon which he bases his

general conclusion and also the source and character of the milk examined by him.

The results secured in our work with the mixed milk of herds of cows and with individual cows of different breeds do not agree with the statement of Blyth. In outline our results were as follows:

(1) The amount of casein varied from 1.93 to 3 per cent., and averaged 2.48 per cent.

(2) The amount of albumen varied from 0.55 to 0.86 per cent. and averaged 0.66 per cent.

(3) For each pound of albumen in the milk the casein varied from 2.6 to 4.9 pounds, the average being 3.76 pounds of casein for one pound of albumen.

All our work goes to show that the relation of casein to albumen in cows' milk is a variable one, and that very rarely does milk contain five parts of casein for one of albumen and not often does the ratio go above four and one-half to one and seldom goes below three to one, while the average is somewhat under four parts of casein to one of albumen.

(2) *The Relation of Fat to Casein and Albumen in Normal Milk.*—The average composition of milk as given in many of our best authorities generally exaggerates the proportion of casein and albumen. Whether this has come from faulty methods of analysis, or the use of too large a factor in converting nitrogen into casein, or from peculiar kinds of cows, it is difficult to say. In nearly all of the older works we find the amount of casein and albumen given in excess of the fat, and in more recent statements the proportion is large. It may be that our cows in New York State do not give milk like cows in other countries, but the fact has impressed me very strongly that our results show that the relation of casein and albumen to fat in milk is not as great as reported elsewhere.

Giving the general average of our results, we have found the fat to be 3.70 per cent., the casein and albumen, 3.14 per cent., or for each pound of casein and albumen there was on an average nearly 1.20 pounds of fat. The lowest ratio found was 1.07 of fat and the highest 1.33 of fat to 1 of casein and albumen. In working with the mixed normal milk of herds,

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we have never found a single instance in which the milk contained more casein and albumen than fat, and, moreover, we have not found a single instance in which the milk contained as much casein and albumen as fat. In working with the milk of individual cows of seven different breeds we have not yet found a single instance where any individual (in normal health) of any breed gave milk for any considerable period of time that contained as much casein and albumen as fat.

(3) *The Relation of Fat to Casein (Excluding Albumen) in Normal Milk of Cows.*—So far as I have been able to ascertain, there are on record outside of the data furnished by the Geneva (New York) Experiment Station no determinations of casein in cows' milk embracing large amounts of milk during an extended period of time; and hence the relation of casein to fat in cows' milk has received little or no attention until recently. In working with the mixed milk of herds of cows for a period of six months we obtained the following results:

(1) In normal milk which contained fat varying from 3 to 4.5 per cent., the casein varied from 1.93 to 3 per cent. The fat averaged 3.70 per cent., and the casein 2.48 per cent.

(2) In no case did normal milk contain less than 1.35 pounds of fat for one pound of casein, or more than 1.74 pounds of fat for one pound of casein, while the average of all was 1.5 pounds of fat for one pound of casein. Over seventy-five per cent. of the individual results were within one-tenth of the average.

(3) In examining the normal milk of individuals of seven different breeds of cows during the past year, we have never found for any extended period that there was less than 1.3 pounds of fat for one pound of casein.

(4) *The Effect of Removing Fat from Normal Milk upon the Relation of Fat to Casein.*—When fat is removed from milk, the milk loses little else in the way of solids. The casein remains essentially undiminished in quantity. Hence, the greater the amount of fat removed the more casein there will be in proportion to the fat left. In numerous experiments made to ascertain the effect of skimming milk upon the relation of fat to casein, it was found that in no case did skim-milk contain more than 1.35 pounds of fat for one pound of casein and this was

in case of a milk which had less than ten per cent. of its fat removed. As a rule, taking average normal milk as found in New York State, we have found that if as much as twenty per cent. of the fat in the milk is removed the resulting skim-milk will contain less than 1.3 pounds of fat for one pound of casein. Now, considering the fact that we have not found any normal milk to contain less than 1.30 pounds of fat for one pound of casein, while the average is 1.50 pounds of fat for one of casein, it would appear that we might make a practical use of this relation of fat to casein for the detection of skimmed milk. Our work makes it appear that if milk contains less than 1.30 pounds of fat for one pound of casein, it has been skimmed. I feel justified in saying that this standard would be found to give true results ten times where the present crude legal standard used in New York State and elsewhere would be found to give correct results once in a case of skim-milk. And this brings me to my next and last topic.

(5) *The Relation of Fat to Total Solids in Normal Milk as Defined by Law.*—The present legal standard of normal milk in New York and several other states requires that normal milk shall contain twelve per cent. of solids, of which three per cent. shall be fat. I am not entirely certain as to where this so-called minimum standard originated, or upon what work done in New York State its adoption there was based; but I have this to say of normal milk as found at present in New York, that in an examination of a large number of samples of mixed milk of herds representing nearly half a million pounds of milk and the product of several thousands of different cows I have not yet found a single instance in which such milk contained at the same time three per cent. of fat and as much as twelve per cent. of solids. Moreover, in examining a large number of samples of milk from individual cows of many different breeds, I have not found twelve per cent. of solids in milk containing three per cent. of fat, unless the animal was in an abnormal physical condition. It is not difficult to see why normal milk containing three per cent. of fat should not contain twelve per cent. of total solids. Normal milk containing three per cent. of fat should contain about 5.50 per cent. of sugar and ash or 8.50



per cent. solids without casein and albumen. If such milk contains twelve per cent. of total solids, then there must be 3.50 per cent. of casein and albumen, that is 3.50 per cent. of casein and albumen for three per cent. of fat, a relation of these compounds, which, as I have previously stated, I have not yet found in normal milk. Only in skimmed milk containing three per cent. of fat should we expect to find as much as twelve per cent. of solids.

*General Summary.*—We may briefly summarize our statements as follows:

(1) The relation of casein to albumen in normal milk is more or less a variable, and not a definite one.

(2) The amount of fat in normal milk is very rarely less than the amount of casein and albumen. On an average there are 1.20 pounds of fat for one pound of casein and albumen.

(3) Average milk contains about 1.50 pounds of fat for one pound of casein (excluding albumen).

(4) The removal of fat from milk reduces the ratio of fat to casein in the resulting skim-milk. When milk contains less than 1.30 pounds of fat for one pound of casein the milk has in all probability been skimmed.

(5) The legal minimum standard, which requires milk containing three per cent. of fat to contain twelve per cent. of total solids, does not agree with the composition of normal milk as found in New York State, since normal milk that contains three per cent. of fat will contain considerably less than twelve per cent. of total solids. The legal requirement would be met with only in skimmed milk.

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### IMPROVED UREOMETER.

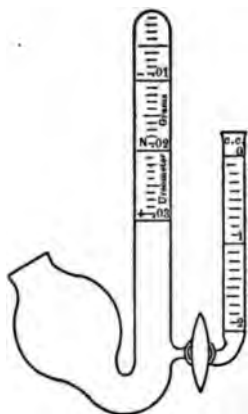
BY PROFESSOR J. I. D. HINDS.

Received October 5, 1893.

IN using the ureometer designed by Prof. Doremus I have found two sources of considerable error. In the first place, it is impossible to run in from the pipette exactly one centimeter of the urine. In the second place, some bubbles of nitrogen almost invariably escape at the bulb of the instrument.

To remove these sources of error, I have devised the appa-

tus shown in the accompanying figure. A tube graduated to tenths



of cc. is attached on the side opposite the bulb, and the two tubes are connected by a stopcock. The instrument is filled with the test liquid in the usual way and then the small tube is filled with the urine. Exactly one cc. is allowed to run in through the stopcock, and then the nitrogen is measured in the larger tube. The instrument gives as great accuracy as can be attained with the small quantities dealt with. The hole in the stopcock should be filled with the urine. This can be done by running in a drop or two of urine

before filling with the test liquid.

The instrument is conveniently held with the left hand while the stopcock is being operated with the right.

CUMBERLAND UNIVERSITY,  
LEBANON, TENNESSEE.

## CHEMICAL CONSIDERATIONS ON THE POTTERY INDUSTRIES OF THE UNITED STATES.

BY KARL LANGENBECK.

Received Nov. 16, 1893.

### PART I.

OUR pottery industries have developed so purely on an empirical basis, that very little of a chemico-technical character has found its way into English literature concerning them.

Our potters are, almost without exception, innocent of chemical knowledge, and American chemists have had little opportunity of working in their manufactories, or have not felt at liberty to publish their experience in such lines of work.

As, however, the diligence of our many geological surveys causes many thousands of clays to be annually collected, described, and analyzed, it is unfortunate that such extensive

work brings industrially no fruit, because the chemists so employed seem to have no knowledge of the potter's needs and present data that even to the pottery expert are valueless, stopping short, as they do, of the point at which their analyses would prove of use.

It is with the hope that this diligent and extensive effort of the chemists of our geological surveys may be directed into serviceable channels, that a description of the main branches of our American pottery industry will be attempted.

The most important domestic products of our markets, are fire clay goods, terra cotta, red ware, yellow ware, stone ware, C. C. (*i. e.*, cream colored), and white granite ware. The manufacture of bone china and to a limited extent of feldspar porcelain have also been begun, but are not as yet, industrially as important as the former.

Concerning the first two classes, fire clay products and terra cotta, it is not the purpose of the writer to consider them in the course of this article; not because they lack interest from the point of view of the chemist, but because the manufacturer of these wares stands in no such need of the chemist, as the manufacturer of glazed wares, and considerations applying to the examination of the raw materials of the latter, apply equally to those of the former.

*Red Ware.*—The simplest and cheapest of glazed pottery is called from its color, "red ware." It is ordinarily formed from the same materials used for making red brick; alluvial mud found in the river valleys and weathered ferruginous shales. It is important that the material contain but little lime, which if present in any considerable amount, destroys the bright red color imparted by the oxide of iron, giving unsightly ware.

At a heat sufficient to melt a wire of pure silver to a bead, the clay should bake so hard, that it can barely be cut with a knife. The specimen baked at that heat should adhere, when touched to the tongue and be of a bright red color.

The clay must be of such composition, that with the hardness attained at the given temperature (from the melting point of silver to not exceeding that of an alloy of seventy-five per cent. silver, twenty-five per cent. gold), it will have practically the

same co-efficient of expansion, and hence bear without fracture, a glass fusible at that heat.

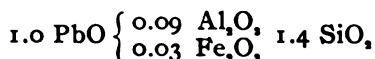
A glass or "glaze" of this character would be one having a chemical formula lying between 1. PbO 0.1 Al<sub>2</sub>O<sub>3</sub>, 1. SiO<sub>2</sub>, and 1.0 PbO 0.15 Al<sub>2</sub>O<sub>3</sub>, 1.5 SiO<sub>2</sub>, made by grinding together

129.7 parts white lead,  
13.0 to 19.5 parts china clay,  
24. to 21. parts quartz.

In order to absolutely resist the action of acids on cooking utensils of "red ware," it would be desirable to use more acid glazes, but such is not the practice in this industry; although there is a practice that should be absolutely condemned and against which chemists should throw their influence, namely, that of using litharge or galena alone as the glazing substance and depending on its taking up sufficient alumina and silica from the body of the ware, during fire, to form the glass. A "glaze" so formed is certain to be basic on the surface, and is sure to be attacked by the weakest acids used in cookery.

The red ware potter has no china clay at his disposal, and usually makes his glaze by grinding the lead preparation with a loamy sand.

The glaze then has frequently some such composition as this—



(taken from practice). This glaze would be of a yellowish color, which is not objectionable.

The co-efficient of expansion of the clay depends on the amount and fineness of the uncombined silica and feldspathic detritus it contains, which constituents, are in the analysis, determined by the "rational analysis" of Seger and Aaron.

A practical "red ware" clay, burning at the indicated temperature to the required hardness and color, and bearing the glaze without suffering fracture ("shivering") or the glaze itself cracking ("crazing"), being of sufficient plasticity and having from the clay to the baked condition a linear shrinkage of one-sixteenth, is a weathered shale of the following analysis:

## 654 CHEMICAL CONSIDERATIONS ON POTTERY INDUSTRIES.

## TOTAL ANALYSIS.

	Per cent.	Insol. in $\text{H}_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3$ .
Silica.....	74.75	57.20
Alumina.....	12.55	0.62
Ferric Oxide .....	5.28	0.70
Lime .....	1.28	0.77
Magnesia.....	0.85	0.00
Alkalies .....	2.27	1.80
Combined Water .....	3.23	
	<hr/> 100.21	<hr/> 61.09

## RATIONAL ANALYSIS.

	Per cent.
"Clay Substance" .....	39.12
Quartz .....	52.54
"Feldspathic detritus" .....	8.55

## PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica .....	44.86
Alumina .....	30.50
Ferric Oxide .....	11.71
Lime.....	1.30
Magnesia .....	2.17
Alkalies.....	1.20
Combined Water .....	8.26
	<hr/> 100.00

The following, a highly plastic red colored clay, proved unsuitable. It was too plastic and would twist and crack in the fire; it burned to a dark brownish red, instead of a light bright color, shrinking one-eighth linear measure in the fire. It contains insufficient uncombined silica to bear a glaze suited to the red ware fire, without the latter's "crazing."

## TOTAL ANALYSIS.

	Per cent.	Insol. in $\text{H}_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3$ .
Silica.....	61.93	28.98
Alumina.....	19.87	0.53
Ferric Oxide .....	7.83	1.57
Lime .....	1.61	0.16
Magnesia.....	0.77	0.08
Alkalies .....	2.38	1.08
Combined Water .....	5.91	
	<hr/> 100.30	<hr/> 32.40

## RATIONAL ANALYSIS.

	Per cent.
Clay Substance.....	67.90
Quartz .....	21.57
Feldspathic detritus .....	10.83

## PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica .....	48.53
Alumina .....	28.48
Ferric Oxide .....	9.22
Lime.....	2.14
Magnesia .....	1.02
Alkalies.....	1.92
Combined Water .....	8.70

The wares manufactured in this industry are flower-pots and other unglazed terra-cotta articles; of glazed articles, brown door-knobs, milk crocks, bean pots, and other cooking vessels, pots for corroding white lead, jardiniers, umbrella-stands, spit-toons, etc., which latter ornamental pieces are often decorated on the outer unglazed surface with oil colors.

The chemist in order to determine the suitability or unsuitableness of a clay for this industry should make a "rational analysis" of the same. He should determine by kneading, in a general way, the plasticity of the material and the coarseness of the admixed quartz.

Cakes several inches square and about  $\frac{3}{8}$  inches thick, should be formed and dried and placed in a muffle with a wire of pure silver; on one or two of the cakes such a glaze-mixture as described before should be painted to the depth of about  $\frac{1}{8}$  inch. The muffle is then fired with a gradually increasing heat until in the course of three hours, the silver wire melts, when firing is discontinued.

It goes without saying that an oxidizing fire must be maintained throughout the burning, in order to insure a bright red color of the clay by complete oxidation of its iron and to prevent a reduction of the lead of the glaze.

When cold the pieces are withdrawn and the color and hardness of the unglazed ("biscuit") pieces and the character of the glazed sherds, and whether in the course of some weeks the latter bear the glaze without defect, are noted.

# CONTRIBUTIONS TO THE STUDY OF OIL-CAKES USED IN FEEDING.<sup>1</sup>

BY C. V. GAROLA.

TRANSLATED AND ABSTRACTED BY DR. G. L. SPENCER, WASHINGTON, D. C.

THESE contributions consist of a series of studies including all the oil-cakes used in the feeding of domestic animals. For the purposes of the Congress the article on cotton-seed oil-cake has been selected for presentation, owing to the general importance of this product.

*Cotton-Seed Oil-Cake.*—Cotton-seed oil-cake is manufactured from the seed of the cotton plant. It is green when fresh, but becomes brown and dark on standing. It usually contains a variable quantity of cotton-seed hulls, dark débris, seed coats, etc. The oil-cakes from cotton-seed may be divided into three classes:

First, those which contain a considerable quantity of filaments of cotton and which are only suitable for use as fertilizers.

Second, those from Egypt and the Levant where the manufacturers clean the seed very thoroughly from the cotton fiber.

Third, oil-cakes manufactured from decorticated seed in America. In these last the hulls are removed from the seeds, hence these cakes are richer and in a more favorable condition for feeding young animals. We have analyzed two of the last named class. These analyses are shown in parallel columns with the results obtained by Décugis and Woelcker:

	Garola.		Décugis.		Woelcker.
	Cotton-seed from Alexandria.	Decorticated cotton-seed.	Cotton-seed oil-cake from Alexandria.	Cotton-seed oil-cake containing some fiber.	Decorticated cotton-seed.
Water .....	12.44	7.78	9.3	9.15	9.28
Nitrogenous matter .....	28.00	47.81	24.1	20.2	41.12
Fat .....	5.86	12.87	6.1	5.3	16.05
Non-nitrogenous extract matter .....	40.64	20.84	54.5	58.6	25.5
Cellulose .....	8.14	3.80			
Ash .....	4.92	6.90	5.96	6.4	8.05
Nitrogen .....	4.48	7.65	3.86	3.4	6.58
Phosphoric acid.....	1.85	3.33	1.62	1.99	6.58
Potash .....	0.98	0.98	1.62	1.99	6.58

<sup>1</sup> Read before the World's Congress of Chemists, August 24, 1893.

The cotton-seed oil-cake from Alexandria is very much esteemed for the feeding of milch cows. It is very advantageous notwithstanding the fact that its cost is a little high. At the time of writing it costs ten francs, fifty centimes, per 100 kilos, f. o. b. cars at Marseilles. We might cite several dairies, where milk is sold, situated in the suburbs of Nancy, where these oil-cakes have given excellent satisfaction.

The older cattle have considerable power for the digestion of cellulose. In my work, "*Alimentation des Animaux de la Ferme*," published by G. Masson in 1887, I have applied the results obtained in the digestion of woody fibers by cattle as given in the works of Haubner, Sussdorf, and Stoeckhardt:

	Per cent.
(1) Paper pulp, very fine.....	72 to 80
(2) Grass, cut at the time of flowering.....	60 to 70
(3) Paper pulp from straw and wood sawdust.....	40 to 50
(4) Spruce sawdust.....	30 to 40

From these experiments, it appears that the filaments of cotton and the fragments of the seed coating do not present any serious inconvenience to full grown cattle. Such oil-cakes, however, should not be permitted to be fed to young cattle. M. Fagot, a distinguished chemist of Ardennes, has reported several fatal accidents to calves, which have followed the feeding of cotton-seed oil-cake from Egypt. One can easily conceive that the stomachs of the young cattle could not easily dissolve the filaments of cotton and fragments of the hard horny seed coat. As these indigestible particles encumber the third stomach and press upon the rennet, these parts are consequently paralyzed in their action.

Oil-cake from decorticated cotton-seed, which has been sold in the form of a coarse meal at a price of seventeen francs per 100 kilograms, seems perfectly suited for the nourishment of young cattle. I have recommended formerly a mixture of equal parts of wheat bran and linseed meal for the first feeding of lambs. This seems still better suited to the feeding of full grown animals for their fattening and the production of milk. Woelcker in 1888 made a decisive experiment upon the comparative nutritive value of oil-cake from decorticated cotton-seed mixed with its weight of corn flour and oil-cake from linseed in



the fattening of cattle. These beef cattle were divided into two lots and weighed at the beginning of the experiment as follows :

	Kilograms.
Lot No. 1.....	1,482
Lot No. 2 .....	1,437

Each of these lots received the same quantity of chopped beet roots, hay, and straw. As a nutritive supplement he fed to the first lot cotton-seed oil-cake and corn flour, while to the second lot he fed linseed oil-cake. In the six months during which the experiment lasted the first lot consumed :

	Kilograms.
Beet roots .....	1,713
Hay .....	457
Straw.....	234
Corn flour .....	660
Cotton-seed oil-cake (decorticated).....	660

These oil-cakes were fed in a ration of 3.6 kilograms per head per day.

The second lot of cattle consumed during the same time :

	Kilograms.
Beet roots.....	1,714
Hay.....	457
Straw .....	234
Linseed oil-cake.....	1,320

The ration per day per head was 6.8 kilograms. While the increase in the weight of the cattle fed on cotton-seed oil-cake (decorticated) with the addition of corn meal was upwards of 222.7 kilograms, it was only 188.9 kilograms with the linseed oil-cake. Each beef had gained in the first case 1.18 kilos, and in the second only 0.96 kilos.

The ration with cotton-seed oil-cake was, however, more economic. At the present prices, the cotton-seed oil-cake costs nineteen francs and the broken corn sixteen francs at the farm ; the concentrated foods distributed in the first lot costs as follows:

Cotton-seed oil-cake: 660 kilograms	$\times 0.19 = 125.40$	fr.
Corn:..... 660	" $\times 0.16 = 105.60$	fr.
Total.....	231	fr.

The linseed oil-cake costs, on the other hand, 19.5 francs per 100 kilograms, or in all for the second lot 257.40 francs.

From this we see that in one case there was a gain in live weight of forty kilograms with the cotton-seed and at the same time a lower expense of 26.40 francs.

The mixture containing the cotton-seed oil-cake (decorticated) and the corn is thus shown to be largely superior to the pure linseed, and, as this latter according to the unanimous judgment of practical men is one of the best oil-cakes, it is incontestable that the cotton-seed oil-cake merits especial esteem for fattening cattle.

I will also point out an experiment of Mr. Eloire (*Progrès Agricole* du 15 Novembre, 1891), where the same two cows were submitted during two successive periods to a feeding experiment with different foods. During the first period the cows each received:

	Kilograms.
Straw .....	6
Hay.....	6
Cotton-seed oil-cake.....	3
Bran .....	0.75

and they gave on an average 12.5 liters of milk containing thirty-seven grams of butter per 1,000, hence each cow furnished 462.05 grams of butter. In the second period each cow consumed the following:

	Kilograms.
Straw .....	6
Hay.....	6
Linseed oil-cake.....	1.5
Bran .....	0.75

The average yield of milk in this case was 11.1 liters of a richness in butter of 33.4 grams. The butter produced per day by each cow was 370.07 grams. One may see that the cotton-seed oil-cake acted in a very marked degree upon the secretion of milk and the production of butter. As was the case with sesame and coprah especially, it augments the quantity of both the milk and the butter. Thus a favorable comparison is shown between cotton-seed oil-cake and that from linseed as given in the experiments of Woelcker and Eloire.

We can not finish this study of cotton-seed oil-cake without calling attention to the excellent results obtained by Mr. Vitalis

in the feeding of milk ewes at Larzac with cotton-seed from Alexandria:

"The experiments which I undertook lasted three consecutive years," says this agriculturist, "upon my flock at Larzac and were conclusive in a high degree. At the beginning of the experiment, in order to take account of the efficacy of the cotton-seed oil-cake, I selected ten milch ewes and gave to each one a daily ration of 250 grams of the broken oil-cake in two meals, that is, 125 grams in the morning and the same amount in the evening. These sheep, which before the trial had received a ration of one kilogram of second crop hay per day, now only received 300 grams. The increase in the yield of milk was sensible even the first days. The ten animals gave a quantity of milk equal to that produced by fourteen ewes feeding upon the ordinary ration of second crop hay. After such manifestly advantageous results I wished to ascertain if possible whether the reverse would be the case. I separated ten other ewes to which I gave the ration of cotton-seed oil-cake and second crop hay that I had given the first lot, and the first lot I placed upon the ordinary food. The milk gradually increased with the new lot of ewes and decreased to the usual quantity with those submitted to the first experiment."

Mr. Vitalis adds that by the use of cotton-seed oil-cake the price of food per ration has been reduced from ten centimes to six centimes.

He has determined in addition that by the use of the oil-cake the wool, washed in boiling water and soda—per cent. raw wool—was increased sensibly. Before the use of the oil-cake the raw wool yielded thirty-six per cent. at the maximum; afterwards, on the contrary, it yielded 37.4 in 1878, 38 in 1879, and 39.8 in 1880. This progression is quite significant.

The results which we have given show what advantage agriculturists may obtain from the use of cotton-seed oil-cake. It remains for us now to describe how this should be fed.

Cotton-seed oil-cake when mixed with boiling water has a disagreeable taste. On this account it should not be distributed mixed with water. It is admitted that the oil-cake should be broken up into rather fine particles without necessarily reducing

it to a powder. It is the hard particles which the ruminating animals object to eating, since they cause diarrhea on account of their indigestibility. This difficulty may be obviated by care in breaking up the oil-cake a week in advance in such a way that it can be softened by absorbing moisture from the atmosphere without molding. One may avoid molding by placing the cake in a well-ventilated granary.

### CONCERNING THE METHOD OF DETERMINING THE MELTING POINT OF BUTTER.<sup>1</sup>

BY ADOLF MAYER.

TRANSLATED BY W. H. KRUG.

**I**N my work on the relation between the constitution of butter fat and the feeding of the milch cows I have been considerably engaged with the determination of melting points, and found it important to make some experiments for the special purpose of determining the best method of carrying out these determinations. This work brought me to the following results, of which each will be accompanied by the experimental figures relating thereto.

1. Narrow tubes give lower melting and higher congealing points than wide tubes, and in this manner temperatures which are nearer together and thus assume an apparently greater accuracy as far as they are related to each other.

Experiments were carried on (1) with a certain butter fat, (2) with a fat of known uniform composition (caprylic acid), (3) with a known mixture of two fats (two parts oleic acid and one part palmitic acid).

The results were:

#### (1) WITH BUTTER.

In tube of 16mm. internal diam.	In tube of 7mm. internal diam.
Melting point.....	40.4°..... 39.9°
After rapid cooling to	
low temperature ..	38.9°..... 38.5°
After slowly warming	36.8°..... 36.4°

Therefore in every case *ceteris paribus* about 1-2°C. lower in the narrow tubes.

<sup>1</sup>Read before the World's Congress of Chemists, Aug. 21, 1893.

## (2) WITH CAPRYLIC ACID.

In tube of 16mm. internal diam.	In tube of 7mm. internal diam.
Melting point.....	30.3°..... 27.3°
After rapid cooling to	
low temperature ..	30.2°..... 26.8°
After slowly warming	29.8°..... 26.4°

The result thus being analogous and at the same time much more manifest with a uniformly constituted fat. The difference amounts easily to 3°C.

## (3) MIXTURE OF OLEIC AND PALMITIC ACIDS.

In tube of 16mm. internal diam.	In tube of 7mm. internal diam.
Melting point.....	38.4°..... 38.0°
After rapid cooling to	
low temperature ..	37.8°..... 37.3°
After slowly warming	37.0°..... 36.4°

The result being in every respect similar to butter, which, as we know, is a mixture of fats.

The explanation of the phenomenon observed is apparent. The melting point when determined in a narrow tube (not so narrow that capillary attraction can exert any material influence) is always found lower because these tubes are more easily penetrated by the temperature of the surrounding liquid which is measured with a thermometer. This action is most manifest with a fat of uniform constitution as here the amount which melts at the same time is very great, causing the immediate absorption of considerable latent heat and permitting the rapid attraction of heat from the surrounding liquid to exert considerable influence. In these experiments we must always keep the fact in mind that in melting point determinations that temperature is noted at which the last particles of fat disappear, so also in the determination of congealing points that temperature at which the first solid particles appear, as it is impossible to obtain as accurate a figure for the first softening or the last stage of solidification. The primary softening and final melting are, however, near together in a uniform fat, while in mixtures where complicated phenomena of solution and supersaturation are important factors this is never the case.

One experiment will suffice to illustrate the higher congealing points obtained in narrow tubes.

## MIXTURE OF OLEIC AND PALMITIC ACIDS.

In tube of 16mm. internal diam.	In tube of 7mm. internal diam.
Congealing point.... 32.3°.....	33.1°
After rapid cooling to low temperature .. 33.1°.....	33.4°

The influence is therefore approximately of the same extent as with melting points. This is naturally exactly explained as before.

2. Lower melting points are always obtained when the fat is warmed slowly than when it is warmed rapidly. The former are without doubt the more nearly correct, as the melting fat has more opportunity to adapt itself and its properties to the conditions opposed by the new temperature. As proof for this statement the figures recorded above may be applied, though they must be arranged somewhat differently. The influence in this case is especially slight for a uniform fat (only a part of a degree) and large for the artificial mixture and the butter fat (several degrees). By a slow warming I mean a rise of 1° in five minutes, while in the other experiments the temperature was raised 1° every two and one-third minutes.

An explanation of this action can be found in the fact that the melting of a chemical compound is a much simpler phenomenon than the melting of a mixture where in reality at the final temperature a still solid body dissolves in the liquefied portion. Solution takes place, however, only on the surface, and thus more slowly, while liquefaction is instantaneous throughout the whole mass. The former process would, therefore, be benefitted by a longer period of time—an assumption which is verified by the results.

3. To obtain good melting points one must be careful that the previous congelation was complete, for which in butter-like substances a cooling to about 10° below the actual congealing point is absolutely necessary. This is especially important in repeated determinations with the same sample when heating and cooling follow each other rapidly.

For the experimental proof of this statement the figures given above are, however, of no value, although I there speak of rapid and extended cooling. The differences there observed disappear when the heating is conducted slowly and carefully, at least

when the melting points are determined as they were in these experiments. If they are determined, however, as I have permitted them to be in other experiments, by the sinking of a drop of water in the sufficiently softened fat, it is self-evident that then the half-soft condition caused by a preliminary melting is not without influence upon the result. This, however, is a circumstance which can not be easily avoided. I have, nevertheless, when making melting point determinations of butters by this method, obtained fairly concordant or at least parallel results with those obtained when I took the mean of the melting and congealing points determined in the manner described.

The experiments were made by Mr. F. J. von Pesch, Assistant at the Station.

ROYAL EXPERIMENT STATION,  
Wageningen, July 10, 1893.

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#### NEW BOOKS.

EXPERIMENTS ON AIR. PAPERS BY THE HON. HENRY CAVENDISH, F.R.S.  
1784-1785. Alembic Club Reprints, No. 3. 12mo. Cloth. 52 pp.  
Wm. F. Clay.

To read Cavendish's papers is inspiring. He did so much with so little. Accuracy in experiment and insight into the causes of phenomena characterize all his work, notwithstanding the phlogiston fog in which he moved. This booklet contains two of his papers both taken from the Philosophical Transactions; the first, read Jan. 5, 1784, relates to his discovery of the composition of water; the second, read June 2, 1785, tells how he discovered the composition of nitric acid by uniting the oxygen and nitrogen of the air by the electric spark. To those who do not have access to the originals this series of reprints will be invaluable.

E. H.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE RELATION OF TEACHING TO RESEARCH IN CHEMISTRY.<sup>1</sup>

BY W. E. STONE.

IT is eminently proper that this Congress of Chemists should devote some portion of its attention to the teaching of the science. This not alone because it is desirable that chemists be well taught, but also by reason of the prominent place chemistry has secured in the curriculum of every college and university as well as in many high schools. The teaching of chemistry in institutions of learning is a modern innovation, introduced and developed within the memory of living men. The chemical laboratory as a means of instruction was first recognized in America about thirty years ago. Now the chemical lecture room and laboratory form an essential part of the equipment of every institution for higher education. It naturally follows that teachers of chemistry have become numerous, and positions of this kind are the goals toward which many young chemists aspire.

The teaching of chemistry has therefore become a kind of profession with its own peculiar limitations and disappointments as well as its pleasures and aspirations. The discussion of methods and details of teaching chemistry I leave to the speakers who are to follow me. I wish, however, to consider briefly what I regard as a most important feature of didactic chemistry, viz.: *The attitude of teachers of chemistry toward research.*

<sup>1</sup> Opening address by the Chairman of the Section of Didactic Chemistry at the World's Congress of Chemists, Chicago, August 26, 1893.



A survey of the field reveals an interesting comparison between America and Europe in this respect. In the European universities we find the teachers of chemistry including the famous investigators and discoverers. It is a recognized function of the teacher that he be also an investigator.

Indeed his appointment to a chair in any of the great universities is dependent upon his standing as an investigator and he retains his position only so long as he maintains this standing. In short one of the necessary qualifications of the teacher is active participation in scientific research. Turning to America, two features are at once noticeable. First, a less degree of activity and attainment in scientific research, and second a weaker interest in the spirit of investigation. We must acknowledge that our teaching and the results of our research are still inferior to those attained abroad. The reasons for this are probably complex, but *chiefly* they are to be sought in the relations of our teachers to investigation. Certainly our teachers of chemistry do not lack training, for many of them have been trained under the conditions abroad which we recognize as superior. They do not lack enthusiasm because many are young men with the successes and examples of their European preceptors still in mind. Our American teachers are not at the head in their profession by reason of any lack of training or enthusiasm or material equipments. If I ask then why, any one of my hearers can answer promptly. Every American teacher of chemistry has a common complaint to voice. They will tell you that the demands made upon them as instructors are alone culpable for their meagre contributions to the annals of research. Too many students. Too many hours of teaching. Too many subjects to be taught. These are the counts in the indictment against the conditions under which our American teachers exist.

In short, to sum up the existing *status*. We find ourselves somewhat in the rear of the foremost ranks of investigators and teachers. We find these branches most flourishing where the activity of the investigator is a required qualification for the teacher. In our own country we find these requirements of secondary moment or they are lost sight of entirely. This seems to me not only a great fault in our educational system, but also a very

serious hindrance to the progress of American chemical science.

I am aware that some will fail to see the relation between teaching and research in chemistry and will maintain that the teacher should be only teaching and the investigator only occupied with investigation.

We may regard this matter from the standpoint of the student, from the standpoint of pure science, and finally from the standpoint of the teacher himself.

The student has a right to expect instruction in chemistry either as part of a liberal education or as preparation for a professional career. In either case it is or should be taught, not as a dead and completed science, but as a constantly advancing vital, living science. It is or should be taught as a science of investigation. The only one who can teach it as such must be himself an investigator. No one would maintain that the discoveries of Wöhler or Hoffmann did in any way detract from their effectiveness as teachers. On the contrary, it is apparent that in their characters as investigators they transmitted an inspiration to their pupils which has given to modern chemistry an incalculable impetus.

Again, science looks mainly to teachers for its advancement, since as a rule, they alone have or should have at command the necessary funds, materials, and equipments for the prosecution of researches. Moreover, they alone have or should have the leisure and unbiased mind so essential in the search for truth.

Lastly, the teacher himself has no right to content himself with the single aim of the pedagog. If he would not stagnate he must advance. He must be himself a student standing as interpreter between the unknown and his pupils. The true attitude of the teacher of chemistry toward research is one of interest and active participation in precisely the same degree as he manifests interest in and sympathy with his pupils.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE; SENT BY H. W. WILEY.—No. 7.]

## THE ESTIMATION OF SUGARS IN CONDENSED MILK.<sup>1</sup>

BY W. D. BIGELOW AND K. P. MCCLROY.

Abstract read before the Washington Chemical Society, February 9, 1893.

**I**N the course of the work with canned goods, which has been carried on in this laboratory during the past year, it was desired to examine condensed milk.

The brands of condensed milk are commonly divided into two classes,—those which contain cane sugar, and those which do not. When cane sugar is absent, milk sugar may be determined by any of the methods which are used for its estimation in fresh milk. In the analysis of condensed milk which contains cane sugar, it has usually been taken for granted that invert sugar was absent. Dr. Wiley, by whose direction this work was undertaken, desired a method for the estimation of the sugars present in condensed milk, which would take into consideration the possible presence of invert sugar. It was at his instance, therefore, that the work which forms the basis of this paper was undertaken. It is not our intention at this time to review all the methods which have been suggested in the analysis of condensed milk, but merely to record some ideas which have suggested themselves and some methods which have been developed in the progress of this work.

Among the methods which have been suggested for the determination of cane sugar in the presence of milk sugar the following may be cited as being the most important:

(1) In the method which seems to be most frequently employed, the total solids are estimated by evaporating a portion of the liquid and drying it to constant weight; casein, fat, and ash are estimated by the ordinary methods; the milk sugar by reduction with an alkaline copper solution; and the amount of cane sugar is obtained by deducting the milk solids from the total solids. Aside from the fact that a "difference" method is never satisfactory, this method is open to the objection that whatever invert sugar may be present is estimated as milk sugar, and the presence of invert sugar is always possible where

<sup>1</sup> Read before the World's Congress of Chemists, Chicago, August 22, 1893.

cane sugar has been used in preserving condensed milk. It is certainly advisable to employ a method which will detect it when present.

(2) The method suggested by Muter<sup>1</sup> is well worthy of attention. In this method, ten grams<sup>2</sup> of the milk are poured on four grams of hydrated calcium sulphate in a basin and evaporated to perfect dryness with frequent stirring so that nothing sticks to the basin. The dry residue is powdered, macerated with ether, thrown on a dry filter over a tared beaker, and percolated with ether until free from fat. The ether is then evaporated off, and the beaker plus fat weighed, from which the percentage of fat is ascertained. The filter and contents are then transferred to a beaker, twenty cc. of hot (not boiling) water added, and the whole well stirred. Thirty cc. of alcohol (sixty per cent.) are then added, and the mixture is allowed to cool with occasional stirring. When cool it is thrown on a filter placed over a long graduated measure and washed with proof spirits (two volumes of water to one of sixty per cent. alcohol) until the filtrate measures 120 cc., at which point the extraction is usually complete. The filtrate is then divided into two equal parts and one portion evaporated in a platinum dish, and then placed in a drying oven at 100° till constant weight is obtained. The weight is then noted, the dish ignited for some time at a dull red heat and again weighed, when the total weight less dish plus ash gives the total sugar, which is multiplied by twenty to get percentage. Evaporate the alcohol from the other portion of the filtrate, wash into a beaker, and determine lactose by means of Fehling's solution. The weight of cuprous oxide thus obtained is multiplied by twenty and calculated from 146 to 100. The amount of milk sugar thus found is deducted from the total sugar, and the result, if over 0.5, is put down as cane sugar. If over 0.5 and under 1.0, a rebate of 0.2 per cent., and if over 1.0 and under 1.5, an allowance of 0.1 per cent., is to be made. But if the amount reaches over 2.0 per

<sup>1</sup> *Analyst*, 1880, 5, 37.

<sup>2</sup> This method is proposed for the examination of fresh milk which has been adulterated with condensed milk. If it is desired to apply it to condensed milk, two to three grams should be taken instead of ten grams, and the corresponding correction made in the method of calculation.

cent. it may be taken as it stands. This method is somewhat tedious, and in general is open to the same objections as the first one cited. It is also found that when a large amount of cane sugar is present considerable difficulty is experienced in the extraction of both sugar and fat.

(3) The inversion of the cane sugar by means of mineral acids: A number of methods have been suggested which may be classed under this head. They are all open to the objection that milk sugar also undergoes hydrolysis when subjected to the action of mineral acids. It has been suggested that a blank containing the same amount of milk sugar as the milk under examination be run with each experiment. This is not practicable, however, as the action of milk sugar under these circumstances is far from uniform.

(4) Shenstone<sup>1</sup> determines both sugars by the aid of the polariscope, milk sugar by copper reduction, and estimates the cane sugar by difference. His method, briefly stated, is as follows: Dilute thirty grams of condensed milk, boil to obtain a normal rotation of the milk sugar, cool, make up to ninety-seven cc. with water, and add three cc. of acid mercurous nitrate. The solution is then mixed by pouring between two beakers, and filtered. One portion of the filtrate is then polarized; this gives the combined readings of sucrose and lactose. Ten cc. of the filtrate are then diluted to 100 cc., and the milk sugar is determined by either Fehling's or Pavy's solution; the combined reading obtained from both sugars less that representing the amount of milk sugar present being equal to the polarization of the cane sugar present. This method has also the disadvantage that it does not indicate the presence of invert sugar. Another objection which may be urged is that inversion is likely to be caused by the nitric acid present in the solution. The author states that if the sugars be determined as soon as possible after the clarification of the milk no inversion can be detected. It is evident, however, that should even a slight inversion occur, a decided error in the amount of sucrose obtained would result. In the first place, the invert sugar would reduce sufficient cuprous oxide to indicate almost

<sup>1</sup> *Analyst*, 1888, 13, 222.

twice its weight of milk sugar. Then, of course, the polarization of the combined sugars would be reduced. Thus, the sucrose would be obtained by subtracting a figure too large for the amount of milk sugar from one too small for the combined polarization of the two sugars.

(5) Stokes and Bodmer<sup>1</sup> have suggested that the cane sugar be determined by inversion with citric acid. The details of their method are as follows: Dilute the milk and place in a burette. Hang on to the lower end of the burette a flask (100 cc.) by means of a rubber tube fitted with a screw clip. The flask should be provided with another tube for the exit of ammonia vapors. Place in the flask forty cc. of Pavy's solution, boil, and gradually add the sugar solution till the blue color disappears. Read the burette. Into another flask containing forty cc. of Pavy's solution run the amount of sugar solution (less two-tenths) found necessary to decolorize in the first experiment, and boil. Should the liquid remain blue, it shows that the first reading was correct within 0.1 cc. Next boil another portion of the diluted milk with citric acid in sufficient amount to form two per cent. of the solution, for ten minutes, cool, neutralize with ammonia and repeat the titration. Cane sugar is completely inverted by boiling with two per cent. of citric acid, while milk sugar is not affected. The reducing power of milk sugar may be taken as being fifty-two per cent. of that of glucose, using Pavy's solution. The dilution of the milk should be such that from six to twelve cc. are required for the titration. This method does not seem to have come into general use, although it has been tried by several and is said to give good results. The invert sugar is not taken into account. Shenstone<sup>2</sup> proposes a modification of the apparatus used by Stokes and Bodmer by which he replaces the ammonia driven off during the operation.

*The Determination of Cane Sugar.*—It is well known that in the inversion of cane sugar by means of acids, the results are greatly influenced by the apparatus used and the details of the operation. For this reason it was thought best to examine the

<sup>1</sup> *Analyst*, 1885, 10, 62.

<sup>2</sup> *Analyst*, 1888, 13, 222.

methods for the inversion of cane sugar by means of invertase.<sup>1</sup> This method was first proposed by Kjeldahl<sup>2</sup> for the estimation of the sucrose in barley and malt. He found that results obtained by its use were more accurate than those obtained by inversion with acids. Later it was used by O'Sullivan<sup>3</sup> for the estimation of sucrose in cereals. In 1890, O'Sullivan and Thompson<sup>4</sup> made a careful study of this method and published an account of their work together with a bibliography of invertase and directions for its preparation.

Instead of preparing the invertase itself as they here directed, we followed the method suggested by them in a later paper<sup>5</sup> and used the yeast liquor obtained by the decomposition of brewers' yeast.

For the preparation of this liquid, brewers' yeast was allowed to stand one month at the temperature of 15°. The product, which was then mostly liquid, was filtered, and for the purpose of preservation alcohol was added till the solution contained ten to twelve per cent. absolute alcohol. The mixture was then allowed to stand for a few days and filtered.

The first series of experiments was made to determine the amount of yeast liquor required to obtain complete inversion. The amount of yeast liquor used varied from one to three cc. and the time was four hours.

About 200 grams of granulated sugar were dissolved in one liter of water. For each inversion fifty cc. of this solution were transferred to a hundred cc. flask. Two of these portions were made up to the 100 cc. mark, and the solutions polarized without inversion to obtain the direct reading. The solution polarized 38.3° on the Schmidt and Haensch half-shadow instrument in a 200 mm. tube. The flasks which contained sugar intended for inversion were placed in a large water bath, the temperature of which was held at 55° throughout the operation. As

<sup>1</sup> Richmond and Boseley (*Analyst*, July, 1893) suggest that this method would probably be suitable for the determination of cane sugar in condensed milk. Our own work, however, was done before that time.

<sup>2</sup> *Meddelelser*, 1881, 337.

<sup>3</sup> *J. Chem. Soc., Trans.*, 1886, 49, 58.

<sup>4</sup> *J. Chem. Soc., Trans.*, 1890, 57, 834.

<sup>5</sup> *J. Chem. Soc., Trans.*, 1891, 59, 46.

soon as the proper temperature was reached the yeast liquor was added. In order to hold the flasks in position in the bath, a frame was constructed of parallel strips placed about one inch apart and small nails were driven at intervals of about two inches along the top of the strips. The necks of the flasks were then placed between these strips and held in position by means of rubber bands which were stretched across between the nails. At the end of four hours the operation was stopped. A little corrosive sublimate was added to the contents of each flask to prevent any fermentation which might be caused by the yeast as the solution cooled. Some alumina cream was also added to assist in the clarification. The solutions were then cooled to about the temperature of the room, made up to the 100 cc. mark, thoroughly mixed by shaking, filtered, and polarized. The result of this experiment is given in table 1.

TABLE 1.

Yeast liquor, cc.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
1	51	9.976	9.690
1	51	9.976	9.664
2	52	9.976	9.846
2	52	9.976	9.820
3	53	9.976	9.898
3	53	9.976	9.768
3	53	9.976	9.716

On examining this table, it will be evident that the amount of cane sugar indicated is too low in every case.

Another series of inversions was then started in which the sucrose solution was of the same strength as in the previous series, though only half as much (about five grams) was taken for each inversion. The direct polarization of one of these portions was found to be  $19.15^\circ$  on the sugar scale. The time allowed was five hours and the amount of yeast liquor used was five cc. The results of this series will be found in table 2, which is given below:

TABLE 2.

Yeast liquor, cc.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
5	30	4.988	5.001
5	30	4.988	4.975
5	30	4.988	4.975
5	30	4.988	5.001
5	30	4.988	4.988
7	32	4.988	5.001



It was also suggested by O'Sullivan and Thompson<sup>1</sup> that brewers' yeast be used instead of invertase or yeast liquor. They directed that fresh brewers' yeast be added to the solution to be inverted to the amount of about one-tenth the weight of the sucrose present. On account of the greater uniformity of ordinary compressed yeast, however, and the ease with which it can always be obtained, a series of inversions was made with it and its action compared with that of the yeast liquor used in the preceding experiments. For this purpose the cane sugar solution was prepared as before, and some portions containing ten, and others containing five grams, were taken for the inversion. The time allowed for this series was four hours. The results obtained by this series of inversions are given in table 3.

TABLE 3.

Yeast, grams.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
1	60	9.976	9.989
1	60	9.976	9.872
1	60	9.976	9.872
2	70	9.976	9.846
2	70	....	....
2	70	....	....
2	45	4.988	4.845
2	45	4.988	4.897

These results are too low. In order to determine whether this is due to the fact that not enough time was allowed for complete inversion, or an insufficient amount of yeast was employed, two more sets of inversions were begun, in one of which (table 4), five grams, in the other (table 5), ten grams, of cane sugar were employed.

TABLE 4.

Yeast, grams.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
1	25	4.988	4.975
1	25	4.988	4.988
1	25	4.988	4.949
2	25	4.988	4.975
2	25	4.988	4.949
2	25	4.988	5.001

<sup>1</sup>*J. Chem. Soc., Trans.*, 1891, 59, 46.

TABLE 5.

Yeast, grams.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
2	50	9.976	9.950
2	50	9.976	9.950
5	50	9.976	9.976
5	50	9.976	10.002
5	50	9.976	9.976
5	50	9.976	9.976

In each case the inversion was allowed to proceed for five hours. Several of the inversions were allowed to proceed for seven hours, and in no case was any destructive action upon the invert sugar evident.

From these results we infer:

(1) That the results obtained by means of compressed yeast compare very favorably with those obtained by the use of yeast liquor, and since this is more readily obtained and is more convenient it is to be preferred.

(2) That the time necessary for complete inversion is five hours.

(3) That while fair results may be obtained with an amount of yeast equal to one-fifth the weight of the sucrose present, the best results are to be obtained with an amount equal to one-half the weight of the sucrose it is desired to invert. It will be remembered that O'Sullivan and Thompson<sup>1</sup> added brewers' yeast to the amount of one-tenth the weight of sucrose which it was desired to invert. This is due to the fact that the per cent. of invertase contained in compressed yeast is less than in brewers' yeast.

The next step was to determine the effect of invertase upon a pure solution of milk sugar. There seems to be no literature upon this subject. Dastre<sup>2</sup> makes the statement that lactose is inverted by the invertive ferment present in yeast. He seems, however, to base his opinion on the fact that lactose disappears in the presence of yeast, and cites no experiment which would seem to justify the statement that this sugar is hydrolyzed.

<sup>1</sup> *J. Chem. Soc., Trans.*, 1891, 59, 46.

<sup>2</sup> *Compt. Rend.*, 1883, 96, 932.

Milk sugar was dissolved in water, the solution boiled to obtain the normal rotation of milk sugar, cooled to room temperature, and portions of fifty cc. each measured into 100 cc. flasks. Two of these were diluted to the mark and polarized. The reading was  $5.2^{\circ}$ . The others were subjected to the action of invertase for five hours at  $55^{\circ}$ , some with yeast liquor, others with compressed yeast. The polarization of the solution before and after the operation is given in tables 6 and 7.

TABLE 6.

Yeast liquor, cc.	Total liquid in cc.	Original polarization.	Polarization after inversion.
1	51	5.2	5.3
1	51	5.2	5.1
2	52	5.2	5.1
2	52	5.2	5.2
2	52	5.2	5.2
3	53	5.2	5.3
3	53	5.2	5.2

TABLE 7.

Yeast, grams.	Total liquid in cc.	Original polarization.	Polarization after inversion.
2	50	5.2	5.1
2	50	5.2	5.3
2	50	5.2	5.3
5	50	5.2	5.2
5	50	5.2	5.0

From these figures we feel justified in saying that the inversion noted by Dastre must have been due to some other cause than the influence of the invertase present in yeast.

The fact being thus established that milk sugar is not affected by the action of invertase, it was next undertaken to invert cane sugar in the presence of milk sugar by this method.

Solutions of the two sugars were prepared of about the same strength as was used in the preceding experiments. About 600 grams of granulated sugar were dissolved in three liters of water. Approximately 100 grams of milk sugar were dissolved in three liters of water. This solution was boiled for some time, and then cooled to room temperature. Fifty cc. of the cane sugar solution diluted to 100 cc. and polarized gave a reading of  $38.2^{\circ}$  on the sugar scale.

In this set of inversions, as in the previous ones, 100 cc.

flasks were used. Into each flask were placed fifty cc. of the sucrose solution and twenty-five cc. of the lactose solution, making about twelve parts of the former to one of the latter. The operation was conducted just as in the inversions of the cane sugar alone, and was allowed to proceed for five hours. The results are given in table 8.

TABLE 8.

Yeast liquor, cc.	Milk sugar, grams.	Total liquid in cc.	Cane sugar added, grams.	Cane sugar found, grams.
1	0.86	76	9.950	9.794
2	0.86	77	9.950	9.898
2	0.86	77	9.950	9.924
3	0.86	77	9.950	9.950
3	0.86	78	9.950	9.924
3	0.86	78	9.950	9.950

In this experiment the amount of yeast liquor used varied from one to three cc. for each inversion. It will be seen from the table that the inversion was not complete in those samples which contained less than three cc. of yeast liquor.

It was then attempted to invert cane sugar mixed with about one-third its weight of milk sugar. For that purpose twenty-five cc. of a cane sugar solution, fifty cc. of a milk sugar solution, of the same strength as was used in the preceding experiments, were transferred to each flask used in this series of inversions. Twenty-five cc. of the cane sugar diluted to 100 cc. and polarized gave a reading of  $19.1^{\circ}$  and contained about five grams of sucrose. After five hours the inversion was interrupted. The results are given in table 9.

TABLE 9.

Yeast liquor, cc.	Total liquid in cc.	Milk sugar added, grams.	Cane sugar added, grams.	Cane sugar found, grams.
1	76	1.716	4.975	4.923
1	76	1.716	4.975	4.975
1	76	1.716	4.975	4.975
2	77	1.716	4.975	4.923
2	77	1.716	4.975	4.949
2	77	1.716	4.975	4.975
3	78	1.716	4.975	4.975
3	78	1.716	4.975	4.949
3	78	1.716	4.975	4.975
3	78	1.716	4.975	4.949

It was next desired to study the influence of compressed yeast on solutions containing both sucrose and lactose in the proportion of twelve of the former to one of the latter. Each portion contained about ten grams of cane sugar. The inversion was interrupted after four hours. In table 10 are given the results of the inversion.

TABLE 10.

Yeast, grams.	Total liquid in cc.	Milk sugar added, grams.	Cane sugar added, grams.	Cane sugar found, grams.
1	85	0.858	9.950	9.820
1	85	0.858	9.950	9.898
1	85	0.858	9.950	9.924
1	85	0.858	9.950	9.820
1	85	0.858	9.950	9.898
2	95	0.858	9.950	9.872
2	95	0.858	9.950	9.898

These results are rather low, probably on account of the fact that sufficient time was not allowed for the complete inversion of this amount of sucrose.

The same amount of cane sugar was then inverted in the presence of twice the amount of milk sugar. The time allowed was in some cases four (table 11), in some, five hours (table 12).

TABLE 11.

Yeast, grams.	Total liquid in cc.	Milk sugar added, grams.	Cane sugar added, grams.	Cane sugar found, grams.
1	100	1.716	9.950	9.898
1	100	1.716	6.950	9.846
1	100	1.716	9.950	9.950
2	100	1.716	9.950	9.794
2	100	1.716	9.950	9.846
2	100	1.716	9.950	9.846

TABLE 12.

Yeast, grams.	Total liquid in cc.	Milk sugar added, grams.	Cane sugar added, grams.	Cane sugar found, grams.
2	100	1.716	9.950	9.898
2	100	1.716	9.950	9.976
2	100	1.716	9.950	9.950
5	100	1.716	9.950	9.924
5	100	1.716	9.950	9.950

The examination of these tables confirms the former experi-

ments with regard to the time necessary for complete fermentation.

In this case, as in all others in which the volume of the liquid was too great to make use of a 100 cc. flask, a 200 cc. flask was used instead, and the reading obtained was multiplied by two.

A mixture of cane and milk sugar was then made, in which the sugars were present in about the same proportion as they are usually found in condensed milk, *i. e.*, three parts of cane sugar to one of milk sugar. Approximately five grams of sucrose were present. The time allowed for this set of inversions was five hours, and the result, as will be seen in table 13, was entirely satisfactory.

TABLE 13.

Yeast, grams.	Total liquid in cc.	Milk sugar added, grams.	Cane sugar added, grams.	Cane sugar found, grams.
1	75	1.716	4.975	4.983
1	75	1.716	4.975	4.949
1	75	1.716	4.975	4.975
1	75	1.716	4.975	4.975
1	75	1.716	4.975	4.923
2	75	1.716	4.975	5.001
2	75	1.716	4.975	4.949
2	75	1.716	4.975	4.975

A sample of whole milk was then taken, fifty cc. introduced into a 100 cc. flask, three cc. mercuric iodide solution<sup>1</sup> and a little alumina cream added, the solution made up to the mark, filtered, and polarized. Similar portions of the milk were heated to 80° to destroy any ferments which might be present, allowed to cool to 55° and treated as before; some with yeast liquor and others with compressed yeast. Some of these were kept at this temperature for four hours, and others for five hours. Then they were clarified as before, cooled, made up to the mark, filtered, and polarized. On examining table 14, it will be seen that, allowing for the usual error of polarization, the milk sugar had not been in any way affected by the action of the invertase. A portion of this milk was diluted to some extent before the portions for inversion were measured out. These, as will be seen by the table, read 6.1° on the sugar scale before inversion.

<sup>1</sup> Potassium iodide 33.2 grams, mercuric chloride 13.5 grams, acetic acid 20 cc., water 64 cc.

TABLE 14.

Yeast liquor, cc.	Total liquid in cc.	Milk, cc.	Polarization before inversion.	Polarization after inversion.	Time in hours.
3	53	50	8.2	8.1	4
3	53	50	8.2	8.2	4
3	53	50	8.2	8.3	4
3	53	50	8.2	8.2	4
3	53	50	8.2	8.2	4
3	53	50	8.2	8.2	4
3	53	50	8.2	8.1	4
3	53	50	8.2	8.2	4
3	53	50	8.2	8.3	4
3	53	50	8.2	8.3	4
3	53	50	8.2	8.2	5
3	53	50	8.2	8.2	5
3	53	50	8.2	8.2	5
3	53	50	8.2	8.1	5
3	53	50	6.1	6.1	5
3	53	50	6.1	6.0	5
5	55	50	6.1	5.9	5
5	55	50	6.1	6.1	5
5	55	50	6.1	6.1	5
5	55	50	6.1	6.2	5

The influence of compressed yeast upon whole milk was next tried. This series is a repetition of the previous one, with the substitution of compressed yeast for yeast liquor. The results are given in table 15.

TABLE 15.

Yeast, grams.	Total liquid in cc.	Milk, cc.	Polarization before inversion.	Polarization after inversion.	Time in hours.
2	70	50	8.2	8.0	4
2	70	50	8.2	8.2	4
2	70	50	8.2	8.2	4
2	70	50	8.2	8.3	4
2	70	50	8.2	8.0	4
2	70	50	8.2	8.2	4
2	70	50	8.2	8.2	4
2	70	50	8.2	8.2	4
2	70	50	8.2	8.1	4
2	70	50	8.2	8.2	5
2	70	50	8.2	8.3	5
2	70	50	6.1	6.0	5
2	70	50	6.1	6.1	5
2	70	50	6.1	6.1	5

From these results it appears that if there is any inversion of milk sugar produced by the action of invertase, the amount must be so small that it can not be detected by the polariscope.

The next step taken was to mix a solution of cane sugar with whole milk, and invert the sucrose in this mixture. For this purpose approximately 400 grams of granulated sugar were dissolved in one liter of water. Twenty-five cc. of this solution diluted to 100 cc. gave a reading of  $39.0^{\circ}$  on the sugar scale. Fifty cc. of the milk which was to be used in this experiment were placed in a 100 cc. flask, clarified as given above by means of mercuric iodide dissolved in acetic acid, and alumina cream, made up to 100 cc., filtered, and polarized. The reading was  $8.2^{\circ}$ . To another fifty cc. of the same milk twenty-five cc. of the cane sugar solution were added, clarified as before, made up to the mark, filtered, and polarized. The filtrate read  $48.2^{\circ}$ . From these figures the volume of the solids precipitated from fifty cc. of the milk was estimated to be 2.5 cc. For the purpose of inverting cane sugar in solution in milk, portions of fifty cc. each of the milk were measured into 100 cc. flasks, twenty-five cc. of the solution of cane sugar were added to each portion, and the mixture treated with yeast liquor in the same manner as in the inversion of sucrose in aqueous solution. As soon as the contents of the flasks had reached the temperature of  $55^{\circ}$ , the yeast liquor was added. This temperature was held constant for four hours. Three cc. of the solution of mercuric iodide in acetic acid and a little alumina cream were then added, the flasks shaken gently, cooled, made up to the mark, filtered, and the filtrate polarized. The results obtained by this method are given in table 16.

TABLE 16.

Yeast liquor, cc.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
3	80	50	10.158	10.054
3	80	50	10.158	10.080
3	80	50	10.158	10.132
3	80	50	10.158	10.132
3	80	50	10.158	9.976

A solution of cane sugar was also made which contained half the amount of sucrose given above. Similar mixtures inverted



as in the preceding experiment for four hours showed that the sucrose was completely inverted, as may be seen in table 17.

TABLE 17.

Yeast liquor, cc.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
3	80	50	5.079	5.079
3	80	50	5.079	5.079
5	80	50	5.079	5.105

A comparison of tables 16 and 17 shows that better results were obtained with five grams of sucrose than with ten grams. It was thought that a five hour inversion would give better results in the presence of ten grams of sucrose. Twenty-five cc. of an aqueous solution containing that amount of cane sugar were added to fifty cc. of milk, and the mixture subjected to the action of yeast liquor for five hours. The results as given in table 18 would seem to indicate that five hours are necessary for complete inversion.

TABLE 18.

Yeast liquor, cc.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
3	80	50	10.158	10.162
3	80	50	10.158	10.158
3	80	50	10.158	10.210
3	80	50	10.158	10.132
3	80	50	10.158	10.162
3	80	50	10.158	10.106
3	80	50	10.158	10.210
3	80	50	10.158	10.210
3	80	50	10.158	10.236
4	80	50	10.158	10.158
4	80	50	10.158	10.184
4	80	50	10.158	10.158
4	80	50	10.158	10.158
4	80	50	10.158	10.080
4	80	50	10.158	10.236

It was next desired to study the influence of compressed yeast on a solution of sucrose in milk. For this purpose about 180 grams of granulated sugar were dissolved in one liter of water and the solution polarized. Twenty-five cc. of this solution were mixed with fifty cc. of milk for each inversion. As in all former cases compressed yeast gave the same result as the

liquor prepared from brewers' yeast had done. The results are given in table 19.

TABLE 19.

Yeast, grams.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
2	75	50	4.611	4.637
2	75	50	4.611	4.585
2	75	50	4.611	4.637
2	75	50	4.611	4.611
2	75	50	4.611	4.585
2	75	50	4.611	4.611

The time allowed for this operation was but four hours, but the amount of sugar in each flask was less than five grams and the inversion was complete.

It was next undertaken to invert ten grams of cane sugar by means of yeast. This amount of granulated sugar dissolved in twenty-five cc. of water was added to fifty cc. of milk, the mixture clarified, made up to the mark, filtered, and the filtrate polarized as before. The reading was  $48.2^{\circ}$ . Fifty cc. of the milk treated in the same way gave a reading of  $8.2^{\circ}$ . The reading of the sucrose added, therefore, was taken as  $40.0^{\circ}$ . At the end of four hours the operation was interrupted. The sucrose found is given in table 20.

TABLE 20.

Yeast, grams.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
2	75	50	10.158	10.132
2	75	50	10.158	10.080
2	75	50	10.158	10.210
2	75	50	10.158	10.158
2	75	50	10.158	10.132
2	75	50	10.158	10.206
2	75	50	10.158	10.132

The time in this case was not sufficient to permit complete inversion.

Other portions of the solutions used in the preceding set of inversions were treated in the same manner, except that the inversion was allowed to proceed for five hours. The results are given in table 21.

TABLE 21.

Yeast, grams.	Total liquid in cc.	Milk, cc.	Cane sugar added, grams.	Cane sugar found, grams.
2	75	50	10.158	10.184
2	75	50	10.158	10.184
2	75	50	10.158	10.184
2	75	50	10.158	10.210
2	75	50	10.158	10.210
2	75	50	10.158	10.158
2	75	50	10.158	10.028
2	75	50	10.158	10.158
2	75	50	10.158	10.210

The comparison of tables 19, 20, and 21, confirms the conclusions drawn from the results of the corresponding work with the liquor from brewers' yeast.

From these experiments it is evident that this method may be applied to the determination of sucrose in the presence of milk with results which are entirely satisfactory.

Four determinations of sucrose in one of our most popular brands of condensed milk gave the following results:

40.0 per cent.    40.0 per cent.    39.9 per cent.    40.2 per cent.

After this article was prepared Richmond and Boseley<sup>1</sup> made the statement that the polariscope could not be used for the examination of condensed milk, because of the effect of the heat necessary to condense the milk on the optical properties of milk sugar. Thus far we have met with no difficulty from this source.

*Milk Sugar.*—The method for the determination of milk sugar which is suggested below is intended to be used only in the presence of invert sugar. It is evident that when this is present the milk sugar can be determined neither by copper reduction nor by polarization.

Under these circumstances the most convenient solution of the problem seemed to be the destruction of the cane and invert sugars by fermentation, and the subsequent determination of the lactose by means of the polariscope, or by the copper reduction method. It is, however, well known that the complete fermentation of sucrose is a difficult thing to accomplish, the trouble being largely due to the lactic ferment which invariably occurs in saccharine liquids fermenting under ordinary circumstances.

<sup>1</sup> *Analyst*, 1893, 18, 141.

It is equally well known that lactose disappears in the presence of common yeast. This is also probably due to the lactic ferment. Certain inorganic acids and salts, especially hydrofluoric acid and fluorides, have the power of preventing the lactic acid fermentation, and of accelerating, retarding, or even entirely stopping the yeast fermentation, according to the amount employed.

Although fluorides have been extensively used for this purpose in breweries and distilleries, no attempt has yet been made to apply their action to an analytical method.

It seemed desirable then to investigate this subject in order to determine whether their action was sufficiently complete to form the basis of an analytical method. Our first experiments were made to determine whether cane sugar could be completely fermented by yeast in the presence of fluorides. About 1,200 grams of granulated sugar were dissolved in water and the solution made up to six liters. One hundred and seventeen portions of this solution of fifty cc. each (each containing about ten grams of sucrose) were placed in flasks with one-half cake Fleischman's compressed yeast, together with amounts of potassium fluoride varying from five to thirty-five mgms. to 100 cc. of the solution.

These flasks were divided into three lots which were designated as lots A, B, and C. Lot A was kept at a temperature of from  $11^{\circ}$  to  $15^{\circ}$ , lot B from  $20^{\circ}$  to  $25^{\circ}$ , and lot C in a room the temperature of which varied from  $15^{\circ}$  to  $35^{\circ}$ .

In each of these lots the flasks were arranged in thirteen sets of three each. The flasks of each set all contained the same amount of fluoride, and a blank containing no sugar was run with each set. One flask from each set was used for qualitative tests with Fehling's solution. The others were polarized.

After standing three days all samples showed heavy copper reduction. After five days all samples of lot A showed heavy copper reduction, while those samples of lots B and C, which contained the lower amounts of fluorides, showed but light copper reduction. Lot C had progressed farther than lot B.

After seven days the fermentation in lots B and C was almost complete. The fermentation in lot B seemed to be the more

favorable. After eight days the Fehling's solution gave but a slight reaction in lot B and but slightly heavier in lot C. On the tenth day lots B and C were polarized and the sugar was found to be entirely destroyed. Lot A required a much longer time for complete fermentation than lots B and C, sugar still being present after three weeks' standing. After twenty-five days, however, the fermentation was complete. From these experiments we conclude:

(1) That it is possible and entirely practicable to completely ferment cane sugar by means of yeast in the presence of potassium fluoride.

(2) That with from fifteen to thirty mgms. of fluoride per 100 cc. of the solution the fermentation is most satisfactory.

(3) That the best temperature for complete fermentation is from 20° to 25°; and

(4) That under these circumstances eight days is sufficient for complete fermentation.

The next step was to determine the action of yeast on milk sugar in the presence of fluorides. Approximately 160 grams of milk sugar were dissolved in one liter of water and the solution boiled for some minutes. One hundred cc. of this solution placed in a 200 cc. flask, filled up to the mark and polarized, gave a reading of 24.4° on the sugar scale. Similar portions of the solution were treated with yeast and fluoride as shown in the table and set aside for a number of days. In this series, however, there were six determinations in each set instead of three as in the preceding set. Beginning with the eighth day these solutions were polarized at intervals of from two to three days. In table 22 are given all the readings which were taken in this series.

TABLE 22.

Lactose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization.	Polarization after 8 days.	Polarization after 11 days.	Polarization after 13 days.	Polarization after 16 days.	Polarization after 18 days.	Polarization after 35 days.
8	..	100	24.4	23.4	22.8	21.6	20.4	....	....
8	15	103	24.4	24.4	24.4	24.0	23.6	....	....
8	20	105	24.4	24.4	24.4	24.2	24.0	....	....
8	30	106	24.4	24.4	24.4	24.3	23.8	....	20.0
8	45	110	24.4	24.4	24.4	24.3	24.0	....	18.6
8	60	112	24.4	24.6	24.4	24.2	24.3	24.2	19.2

As before said, it is usually stated that milk sugar is slowly consumed by common yeast. Our own experiments without the use of fluorides confirm this idea, as is shown in table 22. It will be seen that on the eleventh day the sample which contained no fluoride read  $1.6^{\circ}$  lower than those which contained fluoride. It was also impossible to obtain a good clarification on that day, probably on account of the lactic acid ferment which was growing in numbers and which passes through the filter and renders the filtrate turbid. On the sixteenth day the reading was made only with extreme difficulty, while on the eighteenth day it was impossible to effect a clarification which would enable us to read the solution at all.

The next step was the fermentation of mixtures of cane and milk sugar. Separate solutions of both sugars were made in the same manner as in the two preceding series of experiments. This series was treated just as the previous one except that six grams of sucrose were introduced into each flask with the eight grams of lactose. At the temperature at which these experiments were conducted ( $18^{\circ}$  to  $20^{\circ}$ ) thirteen days were required for the complete fermentation of the sucrose. It is believed that ten days would have been sufficient if the temperature had been kept at about  $25^{\circ}$ . The milk sugar solution used polarized  $24.3^{\circ}$ . All the readings taken in this series are given in table 23.

TABLE 23.

Mgms. K.F. per 100 cc.	Total liquid in cc.	Polarization after 5 days.	Polarization after 8 days.	Polarization after 11 days.	Polarization after 13 days.	Polarization after 16 days.	Polarization after 18 days.	Polarization after 35 days.
..	150	23.1	24.0	23.8	23.8	24.0	....	....
15	154	24.1	23.7	24.0	24.0	24.1	24.0	23.4
20	156	23.4	23.1	24.0	24.3	24.3	24.3	23.1
30	158	23.4	23.4	23.7	24.3	24.3	24.3	23.1
40	162	23.1	23.1	24.0	24.3	24.4	24.3	23.7
55	166	23.1	23.7	24.0	23.8	24.0	24.3	24.3

On examining this table it will be seen that the sample which contained no fluoride, and the one which contained but fifteen mgms., did not reach the polarization of the lactose, for before the fermentation of the sucrose was complete the lactic acid fermentation set in to such an extent as to retard the action of the yeast. On the eleventh day the filtrate from the solution con-

taining no fluoride was slightly turbid; on the thirteenth day the reading could be taken only with difficulty, while on the sixteenth day only an approximate reading could be obtained. On the thirteenth day the filtrate from the solution containing fifteen mgms. of fluoride was slightly turbid, and this turbidity increased with each successive polarization of samples containing this amount of fluoride.

A mixture of ten grams of cane sugar and eight grams of milk sugar was next subjected to the action of yeast in the presence of potassium fluoride. The original polarization of the milk sugar was  $24.4^{\circ}$ . The temperature was held at from  $25^{\circ}$  to  $30^{\circ}$  throughout. The results are given in table 24.

TABLE 24.

Mgms. KF, per 100 cc.	Total liquid in cc.	Polarization after 8 days.	Polarization after 11 days.	Polarization after 17 days.
15	113	24.0	24.2	24.4
25	115	24.3	24.4	24.3
50	120	24.5	24.3	24.4

It is thus evident that the presence of milk sugar does not retard the fermentation of sucrose.

It was next undertaken to ascertain whether anything is present in milk which would interfere with the action of the fluoride. For this purpose a sample of whole milk was taken and divided into portions of fifty cc. each, to which varying amounts of fluoride were added. To each of these portions one-half cake of compressed yeast was added. The polariscopic reading of the milk before fermentation was  $14.4^{\circ}$  on the sugar scale. The readings which were obtained on five, eight, and eleven days after the beginning of the operation are given in table 25.

TABLE 25.

Mgms. KF, per 100 cc.	Original polarization.	Polarization after 5 days.	Polarization after 8 days.	Polarization after 11 days.
0	14.4	..	4.8	2.2
0	13.8	8.0	5.4	1.4
6	14.4	9.6	3.8	3.2
6	14.4	10.2	..	4.8
..	..	11.6	6.0	..

It will be seen that in every case there was a decided decrease in the polarized reading of the solution the fifth day and that this became more apparent the longer the operation was allowed to continue. There is evidently something present in milk which did not occur in the aqueous solution of the pure sugars which prevented in a measure the action of the fluoride in preserving lactose. It will be observed that the destruction of the lactose was less in those solutions which contained fluorides than in those which did not, and that for the first eight days the lactose was better preserved in those solutions which contained the larger amounts of fluorides than in those which contained the smaller amounts.

It was at first thought that there might be germs present in the milk, which would account to some extent for the results obtained in the experiment just cited. For this reason a sample of milk was heated to 80° and kept at that temperature for one hour, raising the temperature at the last to the boiling point for a few minutes. The sample was then allowed to cool and after four hours it was heated again as before. It was then cooled, portions of fifty cc. each were measured out and subjected to the action of yeast in the presence of fluoride as before. The original reading of the milk was 14.4°. After nine days the reading was 50.8°. This indicates that the destruction of milk sugar noted was not due to any ferments present in the milk.

It was then thought that this might be due to the presence of the casein in the milk. To ascertain this, one liter of milk was heated for about thirty minutes with ten cc. glacial acetic acid, filtered, and the filtrate polarized. Portions of this filtrate of 100 cc. each were then introduced into flasks and treated with yeast, and with amounts of potassium fluoride varying from 30 to 120 mgms. per 100 cc. of the solution. In this experiment different degrees of dilution in the filtrate were employed. The polarization of a portion of the clarified milk used in each case is given in table 26, together with the amount of fluoride used and the polarization after a number of days.



TABLE 26.

Mgms. KF, per 100 cc.	Original polarization.	Polarization after 8 days.	Polarization after 18 days.	Polarization after 20 days.
30	13.6	6.4	..	..
50	13.6	6.4	..	..
60	13.6	7.0	..	..
70	10.8	5.6	2.0	0
80	10.8	6.2	1.8	0
100	9.4	7.2	3.6	..
120	9.4	4.8	..	..

It is evident from this table that the amount of milk sugar destroyed was not by any means proportional to the amount of fluorides employed. The milk sugar seems to have been steadily consumed until after twenty days lactose could not be detected by means of the polariscope, although in this case the filtrate was so turbid that a slight error may have been made in the reading.

A sample of milk was then clarified by heating to 80° for one-half hour with a 100 cc. of a normal solution of oxalic acid to each liter. The mixture was then filtered, potassium hydroxide added to the filtrate until the reaction was almost neutral, and again filtered. This filtrate was then subjected to the action of yeast and potassium fluoride with the results given in table 27.

TABLE 27.

Mgms. KF, per 100 cc.	Original polarization.	Polarization after 5 days.	Polarization after 8 days.	Polarization after 14 days.
20	9.9	7.0	..	..
30	9.9	7.8	..	6.2
40	9.9	..	..	5.2
60	9.9	7.8	..	..
0	7.4	5.7	4.9	2.7
40	7.4	6.2	5.4	3.8

When it was desired to polarize samples of this set, they were first clarified by means of the addition of a solution of mercuric iodide in acetic acid, and a little alumina cream, made up to the mark, thoroughly mixed, and filtered. On the addition of the mercury solution a strong evolution of carbon dioxide was observed. It is probable that the potassium oxalate resulting from the neutralization of the oxalic acid was converted into potassium carbonate by the action of the yeast. This, of course, would

soon make the solution alkaline and thus interfere with the action of the fluoride.

A sample of milk was then clarified with glacial phosphoric acid in the same manner as in the preceding experiment, filtered, neutralized, and filtered again. The results as given in table 28 confirm those of the preceding experiment.

TABLE 28.

Mgms. KF, per 100 cc.	Polarization after 5 days.	Polarization after 8 days.	Polarization after 14 days.
30	..	7.1	3.6
40	7.6	7.1	4.4
60	..	8.0	4.6

We were unable to clarify milk in such a manner that the lactose would not be consumed by the organisms present in pressed yeast even in the presence of potassium fluoride. It was next attempted to add to the clarified milk something which would feed the yeast and give it such a start that it might be able to assist in holding the lactic acid ferment in check. Cane sugar seemed to be best adapted for this purpose. A sample of milk was taken and divided into portions of 100 cc. each. To each portion was added ten grams of cane sugar dissolved in fifty cc. of water, one-half cake of yeast and an amount of fluoride varying from six to forty mgms. One portion of the milk was clarified and polarized at the beginning of the operation without the addition of sucrose. The portions fermented were polarized on the eighth, eleventh, and thirteenth days. As will be seen in table 29, the original polarization of the lactose was not obtained in any case.

TABLE 29.

Sucrose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization lactose.	Polarization after 8 days.	Polarization after 11 days.	Polarization after 13 days.
10	6	150	14.4	10.8	10.8	8.4
10	11	150	14.4	11.8	12.0	10.6
10	17	155	14.4	14.0	12.8	11.0
10	23	155	14.4	....	13.8	12.4
10	40	165	14.4	....	....	....

Another portion of milk was sterilized by boiling, allowing to stand for four hours, and again boiling. It was then treated just as in the previous experiment with the same result. See table 30.

TABLE 30.

Sucrose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization lactose.	Polarization after 5 days.	Polarization after 9 days.	Polarization after 14 days.	Polarization after 20 days.
2	40	135	14.4	12.4	10.6	6.4	....
2	40	135	14.4	12.4	11.0	4.8	....
10	0	150	14.4	....	12.2	8.6	6.6
10	40	160	14.4	....	12.8	11.6	6.6

Two liters of milk were then clarified by heating to 80° for one-half hour with twenty cc. of glacial acetic acid, filtered, almost neutralized with potassium hydroxide, again filtered, and cooled to the temperature of the room. This filtrate was divided into several portions, and each portion diluted more or less with water. Each of these was again subdivided into portions of 100 cc. each, and to each of these was added a solution of ten grams of cane sugar in water, one-half cake of yeast, and an amount of fluoride varying from 0 to 100 mgms. per 100 cc. of the solution. Similar portions, of course, were polarized without the addition of sucrose. The result was still unsatisfactory, for before the fermentation of the sucrose was complete the milk sugar had begun to decompose. The results are given in table 31.

TABLE 31.

Sucrose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization.	Polarization after 8 days.	Polarization after 18 days.	Polarization after 20 days.
10	0	150	10.8	9.4	....	....
10	7	150	10.8	10.4	6.0	4.4
10	13	150	10.8	10.8	....	5.3
10	20	155	10.8	10.4	....	....
10	27	155	10.8	10.1	....	....
10	33	160	14.2	13.0	9.0	....
10	40	160	14.2	12.4	....	....
10	47	160	14.8	12.3	7.2	1.8
10	53	165	14.8	12.4	5.5	....
10	60	170	14.8	12.6	6.0	....
10	70	170	9.4	8.6	5.4	1.6
10	80	175	9.4	7.6	5.2	....
10	100	180	9.4	7.9	....	....

A liter of milk was then clarified with oxalic acid, filtered, neutralized, filtered, measured out in portions of 100 cc. each, ten grams of cane sugar added to each portion together with one-half cake of yeast, and a varying amount of fluoride. The

solutions were polarized after eight and fourteen days. On the eighth day the fermentation of the sucrose seemed to be complete, and no decomposition of lactose was evident. On the fourteenth day, however, the filtrates were very dark and the readings could only be taken with difficulty. There was also a very marked decrease in the amount of lactose present. The results are given in table 32.

TABLE 32.

Sucrose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization.	Polarization after 8 days.	Polarization after 14 days.
10	13	150	9.9	10.0	5.1
10	20	155	9.9	9.9	6.8
10	27	155	9.9	9.9	7.4
10	33	155	9.9	9.8	8.8

Two liters of milk were then heated to 80° on the steam bath, and a solution of eight grams of glacial phosphoric acid added and the whole kept at this temperature for one-half hour. At the end of this time it was filtered, neutralized, and filtered again. Portions of 100 cc. each were then measured into 200 cc. flasks, and to each was added a solution of cane sugar containing either five or ten grams of sucrose, as shown in the table, and one-half cake of compressed yeast. A portion of the filtrate was also polarized, and gave a reading of 14.4° on the sugar scale. The flasks which were set aside for fermentation were polarized, as is shown in table 33, after eight, ten, fourteen, and eighteen days.

TABLE 33.


Sucrose, grams.	Mgms. KF, per 100 cc.	Total liquid in cc.	Original polarization.	Polarization after 8 days.	Polarization after 10 days.	Polarization after 14 days.	Polarization after 18 days.
5	30	125	14.4	...	14.4	...	14.0
5	30	125	14.4	...	14.2	14.2	...
5	40	125	14.4	...	14.6	...	14.4
10	40	150	14.4	14.4	...	14.3	...
10	40	160	14.4	14.4	...	14.3	...
10	53	160	14.4	14.4	...	14.3	...

As before stated, any solution whose polariscopic reading was desired was first diluted to 100 cc. or 200 cc. In those cases in which 200 cc. was polarized the reading was multiplied by two, so that in the reading given it is always supposed that the amount of sugar present is dissolved in 100 cc. of water. It is

found that the volume of yeast was not great enough to cause any error. The fermentation of sucrose dissolved in milk whose casein had been precipitated by means of phosphoric acid was repeated several times with the same result in every instance. Whenever five to ten grams of sucrose were present at the beginning of the operation, the sucrose was completely fermented at the end of eight to ten days, while the lactose had not been affected at the end of two weeks.

The details of the application of these methods to the determination of the sugars in condensed milk are as follows:

The entire contents of the can are transferred to a porcelain dish and thoroughly mixed. A number of portions of about twenty-five grams are carefully weighed into 100 cc. flasks. Water is then added to two of the portions, and the solutions boiled to make sure that all the lactose is in solution and possesses the normal rotation. The flasks are then cooled, clarified by means of mercuric iodide dissolved in acetic acid, and alumina cream, made up to mark, filtered and polarized. Other portions of the milk are placed in a water bath and heated to the temperature of 55°. One-half cake of compressed yeast is then added to each flask and the temperature maintained at 55° for five hours. Mercury solution and alumina cream are then added, and the solution is cooled to room temperature, made up to the mark, mixed by shaking, filtered and the filtrate polarized. The amount of cane sugar present is then determined by Clerget's formula. In each case the volume of precipitated milk solids may be estimated by the double dilution method. The reducing sugar is then estimated by one of the copper reducing methods. If the amount of reducing sugar estimated as milk sugar, plus the amount of cane sugar obtained by inversion, would give a polarization equal to that obtained by the direct reading of both sugars before inversion, it is evident that no invert sugar is present, and is not necessary to test farther. If, however, the amount of reducing sugar seems to be too great, invert sugar is probably present, and the milk sugar must be determined, by another method. For this purpose 250 grams of condensed milk are dissolved in water and the solution boiled to secure the normal rotation of the milk sugar. The solution



is then allowed to cool to about  $80^{\circ}$ , a solution of  $3\frac{1}{2}$  to 4 grams of glacial phosphoric acid in water is then added, and the mixture kept at this temperature for a few minutes. The mixture is then cooled to room temperature, filled up to the mark with water, thoroughly mixed by shaking and filtered.

It may be assumed that the volume of the precipitate is equal to that obtained by precipitation with mercury solution. Enough potassium hydroxide is then added to almost but not quite neutralize the free acid, and sufficient water is added to make up for the volume of the solids precipitated by the phosphoric acid. The mixture is then filtered and the filtrate is measured in portions of 100 cc. each, into 200 cc. flasks. A solution containing about twenty mgms. of potassium fluoride, and a half cake of Fleischman's compressed yeast, are then added to each flask and the mixture is then allowed to stand for ten days in a room whose temperature is  $25^{\circ}$  to  $30^{\circ}$ . The flasks are filled up to the mark, and the milk sugar is determined either by copper reduction or by means of the polariscope.

*Invert Sugar.*—The weight of cuprous oxide reduced by milk sugar and invert sugar, less the equivalent of the milk sugar found after fermentation, is due to invert sugar.

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## CHEMICAL CONSIDERATIONS ON THE POTTERY INDUSTRIES OF THE UNITED STATES.

BY KARL LANGENBECK.

Received November 27, 1893.

### PART II.

*Rockingham and Yellow Ware.*—A higher grade of ware, than that last treated is "Rockingham and Yellow Ware;" though belonging to the same ceramic category, namely, "Faience," in that it also consists of a porous body covered with a transparent lead glaze.

It differs from "red ware" in color, and in having a body requiring a higher temperature for its proper burning, so that the glaze is not applied to the freshly formed pieces in their "clay state," but to the once baked or "biscuit" pieces, and is then finished in a second or "glost" fire softer than the first.

## 696 CHEMICAL CONSIDERATIONS ON POTTERY INDUSTRIES.

The clays used for "yellow ware" belong to the class commercially known as second-class fire clays; the same from which common fire brick and such terra-cotta articles as stove and flue linings, chimney tops, garden vases, etc., are made. They are generally the common "buff" or "blue" clays of the coal measures and are widely distributed in all our carboniferous exposures.

A typical clay of this character has the following composition:

### TOTAL ANALYSIS.

	Per cent.	Insol. in $H_2SO_4$ Per cent.
Silica.....	60.50	22.33
Alumina .....	25.53	0.53
Ferric Oxide .....	1.66	0.26
Titanic Oxide.....	0.54	....
Manganous Oxide .....	0.33	....
Lime .....	0.38	0.26
Magnesia.....	1.19	0.07
Alkalies .....	1.76	0.37
Combined Water.....	7.98	....
	<hr/> 99.87	<hr/> 23.82

### RATIONAL ANALYSIS.

	Per cent.
Clay Substance.....	76.05
Quartz .....	19.54
Feldspathic detritus.....	4.28
	<hr/> 99.87

### CHEMICAL COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica .....	50.19
Alumina .....	32.87
Ferric Oxide .....	1.84
Titanic Oxide.....	0.71
Manganous Oxide.....	0.43
Lime.....	0.16
Magnesia .....	1.47
Alkalies.....	1.82
Combined Water .....	10.50

The yellow ware potter is better equipped in machinery than

the red ware potter, and does not, like the latter, prepare his clay by merely soaking it with water and then tread and knead it to a plastic mass of the proper consistence ; but subjects the clay to a regular washing process. Hence the presence of a certain amount of coarse sand and nodules and particles of iron pyrites, very commonly found in all such clays, do not spoil them for his work, as they are removed by the necessary and customary process of manufacture.

This consists in "slipping" the clay in a vat with mechanical stirrers, known as a "blunger," sifting the "slip" through a sixty-mesh wire sieve or a No. 8 silk lawn stretched over a vibrating frame, from which the coarser sandy impurities are thrown, and condensing the "slip" to plastic clay by evaporation or by a filter press.

From this process, it will be realized that the clay must be in such a condition of physical aggregation as to be easily disintegrated or "slipped" by mere stirring in water. A hard clay readily reduced by the elements in "weathering" to such a condition, will also answer the purpose ; but the double shoveling involved in transferring clay from the bank to a weathering flat, and from thence, after six months or a year's exposure to the elements, to the factory, is a trouble the potter avoids if he can.

There is a class of clays, which from their composition are admirably adapted for yellow ware, but have remained completely barred from this use because of their physical character. These are the "flint clays" of which the following analysis is typical :—

## TOTAL ANALYSIS.

	Per cent.	Insol. in $H_2SO_4$ , Per cent.
Silica.....	55.04	16.96
Alumina.....	29.85	0.11
Ferric Oxide.....	1.76	....
Lime.....	0.79	0.12
Magnesia.....	0.57	0.17
Alkalies.....	1.83	0.58
Combined Water.....	10.95	....
	<hr/> 100.79	<hr/> 17.94



## RATIONAL ANALYSIS.

	Per cent.
"Clay Substance" .....	82.85
Quartz .....	16.58
Feldspathic detritus.....	1.35
	<hr/>
	100.78

## PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica .....	45.97
Alumina .....	35.90
Ferric Oxide .....	2.12
Lime.....	0.81
Magnesia .....	0.48
Alkalies.....	1.51
Combined Water.....	13.22
	<hr/>
	100.00

This clay occurs in rocky masses having a conchoidal fracture, the splinters of which are so hard and sharp, that a flying piece, struck off with the pick, will cut the hand or face. It eagerly absorbs water and with a crackling noise, though without noticeable evolution of heat, falls to pieces, yielding a mass of shell-like splinters, though a year's exposure to the weather, while reducing it to a fine sand, fails to produce a workable clay. Simple grinding in water and thickening the resulting "slip," by any convenient method, produces a highly plastic mass, that is readily formed into ware, burns to a bright yellow color, and bears the customary yellow ware glazes with less danger of "crazing" than the before-mentioned and commonly used clay. This latter fact is to be accounted for by the extreme fineness of the contained quartz, more than compensating for the reduced quantity of the same.

The expense of wet grinding a "flint clay" would not be excessive, but the introduction of machinery for the purpose, in so conservative a craft as the one under consideration, would be met with almost stolid resistance.

The first or "biscuit" fire of yellow ware, for hardening the clay pieces, must reach "good biscuit heat," that is a temperature sufficient to bake the clay so hard that it can no longer be cut with a knife, but that the steel leaves a lead-pencil-like

mark on the surface. At the same time, the shard must still be porous and adhere when touched to the tongue.

The temperature of the "biscuit" fire will necessarily, of course, vary with the chemical and physical character of the clay used. The potter determines it empirically by testing-trials of the clay drawn from the kiln, with his knife and tongue.

It is very important that the chemist determine at what heat the clay he is examining attain a "good biscuit" condition, in order that the potter may know whether he can introduce ware made of it into his biscuit kiln along with his old ware. As a kiln of ware represents considerable capital exposed to a risky operation, potters naturally are absolutely opposed to the adoption of new clays requiring different conditions of fire from those already adopted by them; these must dovetail easily at least into their kiln conditions, by requiring the same heat.

For the purpose of such heat tests the most accurate and convenient appliance is the Seger pyrometric cone. The cones are easily used, not influenced by momentary flashes of unequal heats, but melt down at the corresponding average temperature of a certain period of time (which is what determines the character and hardness of the baked product); they accord perfectly with others of the same number, are cheap and if not easily obtained can even be made by the operator himself.

Yellow ware clays reach the required hardness at temperatures varying from the melting points of cones V, to VII, or even VIII.<sup>1</sup>

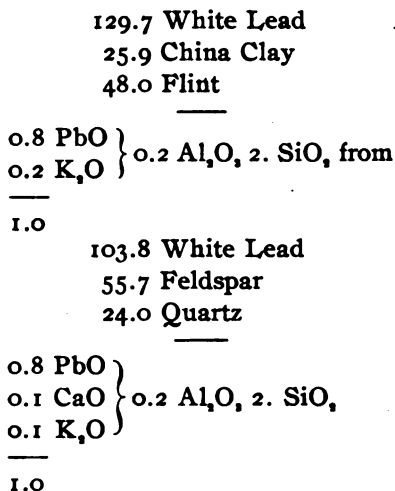
		Per cent.	
V. $\left. \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\}$	$0.5 \text{ Al}_2\text{O}_3 \text{ } 5. \text{ SiO}_2$	Orthoclase.....	83.55
		Marble dust .....	35.00
		Quartz .....	84.00
		Kaolinite.....	25.90
VI. $\left. \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\}$	$0.6 \text{ Al}_2\text{O}_3 \text{ } 6. \text{ SiO}_2$	Orthoclase .....	83.55
		Marble dust.....	35.00
		Quartz .....	108.00
		Kaolinite .....	38.85
VII. $\left. \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\}$	$0.7 \text{ Al}_2\text{O}_3 \text{ } 7. \text{ SiO}_2$	Orthoclase .....	83.55
		Marble dust.....	35.00
		Quartz .....	132.00
		Kaolinite .....	51.80
VIII. $\left. \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\}$	$0.8 \text{ Al}_2\text{O}_3 \text{ } 8. \text{ SiO}_2$	Orthoclase .....	83.55
		Marble dust.....	35.00
		Quartz .....	156.00
		Kaolinite .....	64.75

<sup>1</sup> *Thonindustrie Zeitung*, 1886, p. 169.

## 700 CHEMICAL CONSIDERATIONS ON POTTERY INDUSTRIES.

For "yellow ware" as for "red ware," it is customary to employ a "raw" glaze, that is, one containing no soluble constituents which have first to be rendered insoluble by fritting to a glass.

The customary type of glaze has a formula resembling one of the following: 1.0 PbO 0.2 Al<sub>2</sub>O<sub>3</sub>, 2.0 SiO<sub>2</sub>, which may be made by grinding together:



obtained by grinding together:



The acidity of the glaze generally varies from 1.8 to 2.2 SiO<sub>2</sub>, depending upon the amount of quartz contained in the clay upon which it is expected to stand. The alumina will similarly vary from 0.16 to 0.2 and over according to the stiffness of the glaze required and the conditions of firing, causing a liability to devitrification, or most likely as chance has thrown a fairly satisfactory formula into the potter's hands.

The temperature at which the glazes run bright lies about at a point at which an alloy composed of

50 per cent. Silver

50 " " Gold

will melt, though depending upon the composition of the glaze, and the length of fire, the melting point of the alloy,

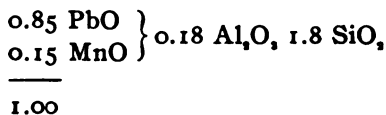
75 per cent. Gold

25 " " Silver

may have to be reached.

"Rockingham ware" differs from "yellow ware" only in that it is covered with a brown manganiferous glaze, applied either by spattering the piece, previously dipped in the clear glaze, with the same, thus producing a mottled effect by the melting of the glazes into each other, or by directly dipping the biscuit piece into the "Rockingham" glaze alone, whereby the fired piece obtains a uniform red-brown finish.

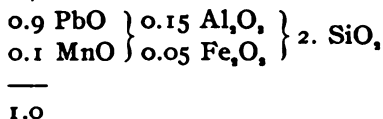
Common forms of Rockingham glazes are the following :



made by grinding together :

110.0 White Lead  
6.5 Black Oxide of Manganese  
23.3 China Clay  
43.2 Flint

also,



similarly prepared with a ferruginous clay, the formula of which any chemist will be able to figure out from the equivalent proportions given.

As in the case of "red ware" the prevailing fire of both the biscuit and glost kilns should be oxidizing.

The ware manufactured in this industry embraces such kitchen and other domestic utensils as bowls, bakers, nappies, chambers, tea and coffee pots, pitchers, etc.

In examining a clay for its possible use in this manufacture it is important to determine whether it can readily be disintegrated by stirring or boiling in water, or whether repeated soaking and drying or freezing and thawing it bring it to such a state.

A "slip" of the clay should be run through a sixty mesh wire sieve and the amount and character of the remaining sand given.

If the latter is at all appreciable the sample for analysis should not be taken from the crude clay, as this would, of course, give an entirely false idea of the constituents ultimately entering the potter's "body," but the sample should be taken from the thickened and dried "slip" which has passed the sixty mesh sieve. Such a "slip" is readily thickened by pouring it on a thick, clean, and dry slab of plaster paris, which readily absorbs the water and from which the plastic clay is readily peeled without danger of contamination with plaster.

A part of the now plastic clay is dried for preparation of the sample for a "rational" analysis, in the customary manner. The bulk of the washed product is formed into cakes and rings for the burning. The latter are made for the purpose of watching the progress made by the clay in the fire, and determining when the baking is finished. These rings should be of such size, as to be readily withdrawn from the muffle with a stout iron wire, through the spy-hole in the door of the same.

When the clay pieces are bone-dry, they are placed in the muffle on a thick bed of clean quartz sand or a thick fire-clay tile strewn with the same.

The rings should be so placed as to be easily reached through the spy-hole in the door brick and parallel with them the Seger cones V, VI, VII, and VIII, should be set upright on a piece of tiling or flat cake of baked or raw clay, to which they had best be stuck with a little "slip." The door brick is then luted in place with a wad of soft clay, and the firing begun gradually, raising the heat at an increasing rate.

Should there be difficulty in seeing the pyroscopes when the muffle has reached bright redness, on removing the plug from the spy-hole, the careful introduction of a thick iron wire in their

neighborhood, will momentarily so far reduce their temperature as to make them clearly discernible against the bright walls of the muffle.

When cone V crooks over, the first clay ring should be drawn from the muffle with a wire and when cool, tested with the knife for hardness, if insufficient the firing is continued until cone V has melted down completely, when the second ring is drawn. The next trial is drawn at the crooking of cone VI, and so on until a heat is reached at which the clay trial ring is sufficiently hard to resist cutting with a knife, without having lost all porosity, adhering when touched to the tongue.

When this heat is reached the firing is discontinued and the furnace allowed to cool.

The fired pieces of clay removed from the cold muffle are covered on one side with one of the described glazes, of which I would recommend the first, which is easily made and fired as a convenient empirical standard, against which to test the coefficient of expansion of the baked clay.

The pieces are then baked a second time to melt the glaze upon them, the heat reached being that of the melting point of the alloy,

50 per cent. Silver,  
50 " " Gold.

It is also very convenient to use the small baked trial rings partly covered with the glaze as trials for this fire, the firing being discontinued when the glaze on one of these rings drawn from the muffle has run bright.

The color of the clay under the clear glaze should be described. Tints approaching bright straw and lemon yellows are the ones sought after. Brownish and reddish tints are not acceptable to the trade buying the ware.

The behavior of the glaze on the clay must also be given. From these data the potter will be able to determine whether the acidity of his glaze must be increased or diminished, or which clays to mix, if he chooses to keep the glaze as it is and compensate the incorrect coefficient of expansion of the clays by mixing them.

## THE SYNTHESIS OF POLYHYDRIC ALCOHOLS BY MEANS OF FORMALDEHYDE.<sup>1</sup>

BY H. HOSÄUS, P. RAVE, P. WIGAND, AND B. TOLLENS.

### I. INTRODUCTION.

BY B. TOLLENS.

THE aldehyde of formic acid or of methyl alcohol, the formaldehyde  $\text{CH}_2\text{O}$ , which can be easily obtained in large quantities, and which at present is assumed to furnish the sugars in the vegetable kingdom by polymerization, is a very favorable material for the synthetic formation of polyhydric alcohols.

Formaldehyde possesses the property when added to other aldehydes or ketones in the presence of calcium or barium hydroxide of combining directly with these, forming compounds in which one or more primary alcohol groups (methyl according to the Geneva nomenclature) are present.

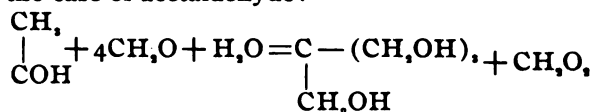
According to the experiments carried out by the above gentlemen and myself the carbon atoms combined with the aldehyde group  $\text{COH}$  or the ketone group  $\text{CO}$  of the bodies acting upon formaldehyde react by combining with as many  $\text{CH}_2\text{O}$  groups as there are hydrogen atoms united to them.

Probably formaldehyde and water form methylen glycol  $\text{CH}_2(\text{OH})_2$ , and this condenses with the aldehydes or ketones with the separation of  $\text{OH}$  and  $\text{H}$  or water.

Thus  $\text{CH}_2$  and  $2\text{CH}_2\text{O}$  form  $\text{C}(\text{CH}_2\text{OH})_2$  and  $\text{CH}$ , with  $3\text{CH}_2\text{O}$  forms  $\text{C}(\text{CH}_2\text{OH})_3$ .

At the same time the aldehyde group  $\text{COH}$  becomes  $\text{CH}_2\text{OH}$  and the ketone group  $\text{CO}$  becomes  $\text{CHOH}$ . There are therefore two more atoms of hydrogen taken up, another portion of formaldehyde forming formic acid with the decomposition of a molecule of water.

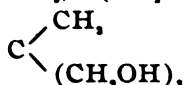
As a result of these changes the following reaction takes place in the case of acetaldehyde:



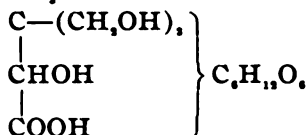
<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

a body being formed which contains four  $\text{CH}_2\text{OH}$  groups combined with one carbon atom or  $\text{C}(\text{CH}_2\text{OH})_4$ .

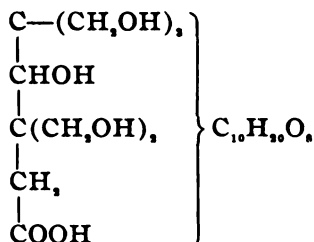
Propionaldehyde,  $\text{CH}_3\text{CH}_2\text{COH}$  in which the carbon atom which is linked to the aldehyde group is combined with only two hydrogen atoms, forms  $\text{CH}_3$ ,  $\text{C}(\text{CH}_2\text{OH})_2$ ,  $\text{CH}_2\text{OH}$  or



Pyrotartaric acid  $\text{CH}_3\text{CO}\cdot\text{COOH}$  forms

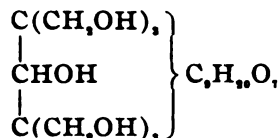


Levulinic acid,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , combines, as it contains a carbon atom with three hydrogen atoms and another with two hydrogen atoms linked to CO groups, with  $5\text{CH}_2\text{O}$  groups forming



The bodies thus formed from pyrotartaric and levulinic acids with formaldehyde are on account of the presence of the carboxyl group still acid and are further decomposed with the separation of water forming lactones or anhydrides. Thus pyrotartaric acid gives  $\text{C}_4\text{H}_8\text{O}_5$  and levulinic acid  $\text{C}_{10}\text{H}_{18}\text{O}_7$ . (See below).

Acetone,  $\text{CH}_3\text{CO}\cdot\text{CH}_3$ , probably takes up  $6\text{CH}_2\text{O}$  groups and forms



or better according the analyses so far made  $\text{C}_8\text{H}_{16}\text{O}_8$ , a hepta-



tomic alcohol with nine carbon atoms which is partially an anhydride.

The reaction of formaldehyde upon aldehydes and ketones above described is probably general in the alcohol and fatty acid series and we are at present engaged in a further investigation which will no doubt furnish a greater number of polyhydric alcohols and alcohol acids.

## II. DESCRIPTION OF THE PRODUCTS ABOVE MENTIONED.

### (a) *Pentaerythrol*, $C(CH_2OH)_4$ . (*Tetramethylolmethane*).

BY B. TOLLENS, P. WIGAND, AND P. RAVE.

This very interesting compound, which was first prepared some years ago<sup>1</sup> but has been investigated only lately crystallizes very beautifully and is formed by mixing

600 grams formaldehyde (32.4 per cent.),  
60 grams acetaldehyde,  
160 grams calcium hydroxide,  
and 9 liters water.

The mixture is allowed to stand several weeks with frequent shaking. The liquid is then decanted, the calcium removed by precipitation with oxalic acid and upon evaporation and separation of the syrup from the crystals by filtration about 115 grams of crude pentaerythrol are obtained.

This is purified by repeated crystallization and extraction with alcohol and then melts at 250–255°. It shows all the properties of a tetrahydric alcohol with five carbon atoms, so that we chose the above name for it as an empirical homologue of erythrol.

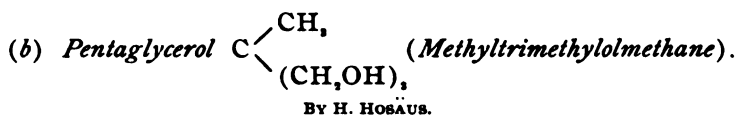
As tetrahydric alcohol it forms a tetracetate and tetrabenzoate, with hydrobromic acid and a tri- and tetrabromhydrin, with hydriodic acid a di-, tri-, and tetraiodhydrin which all crystallize well and show definite melting points.

With nitric acid and with chromic acid it is decomposed and furnishes among other products glycolic acid but no acetic acid. With iodine and sodium hydroxide it does not form iodoform.

From these reactions and the fact that it does not form a secondary iodide with hydriodic acid (as for instance mannitol forms secondary hexyl iodide) we reason that the carbon atoms

<sup>1</sup> *Annalen der Chemie*, 265, 315; 276, 58.

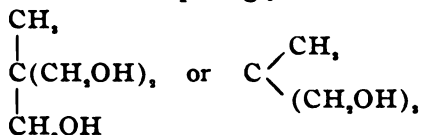
in pentaerythrol are not regularly linked but that it possesses the structure of a methane in which the four hydrogen atoms are replaced by four  $\text{CH}_2\text{OH}$  groups.



When

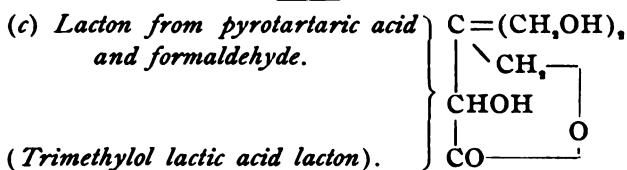
20 grams propionaldehyde,  
 80 grams formaldehyde (40 per cent.),  
 1100 grams water,  
 and 50 grams calcium hydroxide

are heated on the water bath, pentaglycerol is formed.



The liquid is decanted, the dissolved lime precipitated with oxalic acid and the filtrate evaporated to a syrup which slowly crystallizes. The crystals show after purification the melting point  $199^\circ$  and prove to be a trihydric alcohol with five carbon atoms. Pentaglycerol upon distillation in vacuo yields at  $165^\circ$  a triacetate and a tribenzoate.

When oxidized with chromic acid it yields acetic acid and this proves that it contains a methyl group.



BY H. HOSÄUS.

By warming

27 grams pyrotartaric acid,  
 90 grams formaldehyde (40 per cent.),  
 70 grams calcium hydroxide,  
 and 1450 grams water

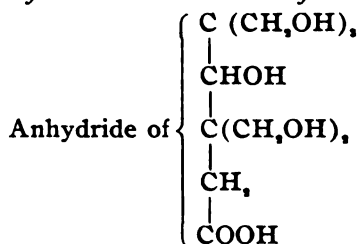
there is formed the calcium salt of a lactic acid in which three hydrogen atoms are replaced by three  $\text{CH}_2\text{OH}$  groups and by precipitation of the calcium with oxalic acid and evaporation of

the filtrate this acid is changed into its lacton. After purification the crystals melt at  $184^{\circ}$ .

This lacton which is neutral regenerates the acid when boiled and combines with 1 molecule of NaOH or  $\frac{1}{2}$  molecule of CaO.

It does not react with iodine and sodium hydroxide nor with phenylhydrazin and therefore does not contain any pyrotartaric acid.

(d) *Lacton from levulinic acid and formaldehyde.*



BY P. RAVE AND B. TOLLENS.

We obtained the barium salt of this acid by allowing

50 grams levulinic acid,  
250 grams formaldehyde (40 per cent.),  
200 grams crystalline barium hydroxide,  
and 5 liters water

to stand fourteen days with frequent shaking, then heating, carefully precipitating the barium with sulphuric acid and evaporating the filtrate. From the syrup we obtained the lacton  $\text{C}_{10}\text{H}_{14}\text{O}_6$ , crystallizing in small plates melting at  $174-176^{\circ}$ , the formula being controlled by Raoult's method.

This compound reacts neither with iodine and sodium hydroxide nor with phenylhydrazin therefore containing no levulinic acid. It is almost neutral but combines with one molecule of NaOH on boiling. It is derived from hydrogenized levulinic acid or hydroxy-valerianic acid, being anhydro-pentamethylol-hydroxy-valerianic-acid-lacton and formed from the above acid by the loss of  $2\text{H}_2\text{O}$ .

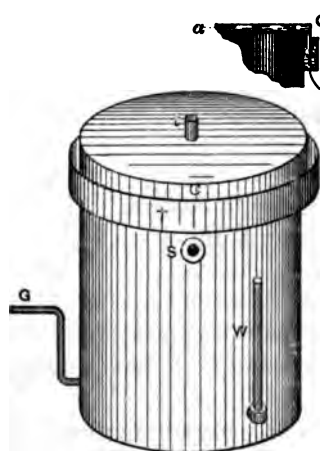
When of the six hydroxyls contained in the above formula one forms a lacton by combining with the carboxyl with separation of  $\text{H}_2\text{O}$  and two others unite in a manner similar to an ether, only three hydroxyls remain, and it is a fact that upon heating this lacton with acetic anhydride three acetyl groups are introduced, a well crystallizing triacetate of the lacton being formed.

## A DRYING OVEN FOR DRYING IN HYDROGEN AT THE TEMPERATURE OF BOILING WATER.

BY F. W. MORSE.

Received September 28, 1893.

THE following described oven has been in use in the laboratory of the New Hampshire Experiment Station for over a year, and proves to be efficient for drying substances in an atmosphere of hydrogen at the temperature of boiling water. It consists of a cylindrical copper box with double bottom and



wall. The inside of the oven is seven inches in diameter and nine inches in depth. The space between the walls is one inch. It is fitted with a water-gauge, W, and a steam outlet, S. This outlet is a screw-nipple, and may be coupled to a condenser if desired. The hydrogen enters the oven by means of a brass tube, G; which is coiled in the space between the bottom and wall and enters the inner oven near the top. The gas is thus thoroughly heated before entering the drying compartment. The gas

passes out of the oven near the bottom by an outlet not shown in the cut. The oven is made gas-tight by a mercury seal. A copper trough, T T' is fitted around the top of the oven a little below the rim. The trough is one and one-fourth inches in depth and one-half inch in width, and is made with brass joints and coated on the inside with lacquer. The cover, C C', fits loosely in the trough, and the mercury, M, makes a perfectly tight joint. Drying is hastened by placing an acid dish containing concentrated sulphuric acid on the bottom of the oven. A rack rests upon the acid dish to receive the watch glasses or drying flasks.

In addition to heating the gas, the oven is made more efficient by blackening the inner walls to increase radiation, and

lining the under side of the cover with a thick sheet of asbestos. The outside of the cover is plated with nickel which diminishes radiation outward. Repeated trials with a standard thermometer inserted in the oven at  $t$ , and between the walls at  $S$ , have shown a difference of only two-tenths of a degree between the boiling water and the drying compartment. Trials with several ordinary chemical thermometers have shown a variation from  $99^{\circ}$  C. to  $101^{\circ}$  C. in the oven.

The oven was made for the Experiment Station by Richards & Co., of New York.

NEW HAMPSHIRE EXPERIMENT STATION,  
DURHAM, N. H.

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### AN IMPROVED GOOCH CRUCIBLE.

BY W. A. PUCKNER.

Received November 14, 1893.

SOMETIME ago I adopted a slight improvement in the use of the Gooch crucibles with which I am so well pleased that I wish to call attention to it.

It is an occasional, if not frequent, occurrence, that while pouring a precipitate on the asbestos, this becomes loose, and floats in the liquid, thus allowing the precipitate to pass through the perforations.

Another objection, which is sometimes urged against this method of filtration, is that the asbestos becomes mixed with the precipitate making an examination regarding purity difficult.

My modification consists in placing a perforated platinum plate, such as are used in the Gooch crucibles made of porcelain, and which may be obtained separately, on the layer of asbestos. This layer need be but very thin as there is now not the least danger of disarranging it while pouring on the liquid. After drying or ignition the precipitate can be obtained perfectly clean and with the loss of but a few milligrams.

HEIDELBERG UNIVERSITY.

## PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

*Ore Separators, etc.*—508,679, November 14, Carter, C., stamp mill and amalgamator. 508,008, November 7, Gelien, G. A., ore grinder. 508,542, November 14, Greer, R. C., ore roasting furnace. 508,381, November 7, Giroux, J. L., smelting furnace. 509,450, November 28, Rushforth, A. P., cupola or blast furnace. 509,439, November 28, Mace, G. A., lime-kiln. 509,550, November 28, Nickerson, T. K., lime-kiln. 508,282, November 7, Clancy, W., apparatus for screening and concentrating ores. 509,818, November 28, Lockhart, W. S., washing and separating minerals, jigging apparatus.

*Gold and Silver.*—509,289, November 21, Bohm, W. D., apparatus for separation of gold from ores. 509,368, November 28, Engelhardt, E. C., treatment of ores; bromine, hydrochloric acid, and sodium carbonate are reagents used.

*Lead.*—508,115, November 7, Noad, J., white lead and colored pigments; float lead is treated with a solution of glycerol and acetic acid and carbon dioxide is admitted. 509,057, November 21, Waller, E., white lead; native lead carbonate heated with ammonium acetate solution is distilled, ammonium carbonate is condensed, and solutions of this and lead acetate are mixed. 509,058, November 21, Waller, E., and Sniffin, C. A.; argentiferous lead carbonate ores are concentrated by dissolving lead in acetic acid and boiling neutral acetate solution to convert into basic lead acetate, while silver is concentrated in the insoluble residue. 509,059, November 21, Waller, E., and Hinman, B. C.; white lead is precipitated from a basic lead acetate solution by dissolving carbon dioxide in water under pressure and forcing basic acetate into tanks.

*Copper.*—509,619, November 28, Helbig, P., hardening copper; melted copper is treated with glass and subcarbonate of iron and antimony is added. 509,633-634, November 28, Tuttle, D. K., and Whitehead, C.; slimes from refined copper are treated with dilute acid then with sulphuric acid or silver sulphate.

*Aluminum.*—508,796, November 14, Ackerman, W., aluminum fluoride; aluminum silicate is treated with hydrofluoric acid.

*Antimony.*—509,478, November 28, Mayer, T.; antimony oxide is dissolving in thirty-three per cent. hydrochloric acid and sixty-seven per cent. hydrofluoric acid and an alkali sulphate is added forming  $2\text{SbF}_6$ ,  $\text{M}_2\text{SO}_4$ , readily soluble in water.

*Acids and Alkalies.*—509,664, November 28, Howard, H., automatic regulator for concentrating sulphuric acid. 508,804, November 14, Blackmore, H. S., electrolysis of salts of alkalies. 508,915, November 21, Cardozo, D. P. F., manufacture of salt; jets of air are forced into brine to concentrate it, the liquid is then transferred to another tank to deposit im-

purities, and then to a third tank and evaporated by air. 508,241, November 7, Richardson, J. C., electrolytic apparatus for the fixed caustic alkalis from sodium and potassium chlorides. 509,163, November 21, Helmer, N., ozone; prepared by adding hydrogen peroxide to a potassium carbonate solution.

*Fertilizers.*—508,220, November 7, Greenstreet, C. J.; nitrogenous fertilizer; tank water or stock is combined with a salt of manganese or iron.

*Sanitary Chemistry.*—509,560, November 28, Sprague, A. V. M., sterilizing apparatus.

*Brewing and Distilling.*—508,882, November 14, Hornbostel, C.; fermented and distilled liquors are treated with kieselguhr. 508,913, November 21, Burkhardt, A. G., apparatus for distilling and rectifying.

*Bleaching and Dyeing.*—508,261, November 7, Weldon, L., apparatus for dyeing. 507,995, November 7, Clegg, C. T., apparatus for bleaching and dyeing. 509,431, November 28, Graemiger, A. and J., apparatus for dyeing. 508,592, November 14, Austen, P. T., friable coloring matter obtained from dye-wood extracts by incorporating ammonium carbonate. 509,703, November 28, Taylor, A., extract from red-wood tree by treating with water and caustic alkali, neutralizing and precipitating solid matters. 509,635, November 28, Ulrich, M., and Bammann, J., brown tetrazo dye. 509,623, November 28, Lauch, R., brown dye,  $C_{13}H_9N_3O_6$ ; made by treating with nitrous acid the compound resulting from action of diazotized amido hydroxy carbonic acid on resorcinol, or orcinol.

*Tanning.*—508,281, November 7, Chailly, F., tanning apparatus.

*Organic Compounds.*—509,087, November 21, Majert, W., piperazine. 509,055, November 21, Thoms, H., salicylate of orthotolyl dimethylpyrazolon,  $C_{12}H_{14}N_4O_3$ . 509,520, November 28, Fritsch, Paul, salicylic ester of acetol; made by heating a salicylate of an alkali and monohalogen acetone and separating the alkaline chloride from acetol formed. 508,124, November 7, Turgard, H. D., denitrating nitro-cellulose by immersing in ammonium hydrosulphate and a metallic sulphide.

*Sugar.*—509,749, November 28, Morrell, J. A., process of and apparatus for evaporating cane juice. 508,747, November 14, Pellegrini, J. E., synthetic sugar; four parts of carbon dioxide, four parts of ethylene, and three parts of water are united by osmose.

*Oils and Varnishes.*—508,479, November 14, Kayser, A., hydrocarbon oils are deodorized by treating dried vapors with anhydrous nitric acid.

*Plaster and Cement.*—508,033, November 7, Mohle, A., artificial stone; sulphuretted slag, brick dust, waste sandstone, sand, cement, and sodium carbonate are used. 508,731, November 14, Majewski, H. A., artificial marble made from calcium sulphate, potassium sulphate, and a solution of alum. 509,428, November 28, Edison, T. A., composition brick; powdered rosin and petroleum are added to ore and heated to expel petroleum, while part of the rosin combines with the metallic oxide to form a resinate.

*Miscellaneous.*—509,396, November 28, Pennington, John C., retting bath for flax, composed of water, caustic potash, ammonia, sodium phosphate, magnesium sulphate, and manganese chloride. 508,015, November 7, Hoffman, H., removing bitterness from kola powder by treatment with hydrogen peroxide. 509,617, November 28, pharmaceutical compound; made from three parts of iodine and one part of meta cresotinic acid. 508,608, November 14, Etheridge, R. L., rosin, made by distilling crude turpentine and bluing. 509,209, November 21, Draper, J., scale is removed from boilers by a composition of water, mercury, sodium, or potassium, and sodium carbonate under heat and pressure. 509,280, November 21, Ash, T. M., to coat non-metallic articles; first cover, with a carrying medium and finely divided metal then treat with silver nitrate. 508,560, November 14, Briersdorf, P. C., treatment of gutta serena, treating with solvent to obtain uniform qualities. 509,460, November 28, Weinrich, M., revivifying spent bone black by impregnating with hot solution of gelatin, drying and charring. 509,589, November 28, Watel, E., process for purifying fatty matters, remaining after essential oils are extracted. 508,469, November 14, Cross, A. K., crayon for polished surfaces; composed of "ozokerite, coloring matter, glycerol, agar, and soapy materials." 508,777, November 14, Stearns, T. C., toilet soap; made from soap stock with sufficient almond meal to neutralize free alkali. 509,049, November 21, Schicht, J., soap; caustic alkali is heated to 135°C., fat is heated separately to 100°, and the heated fat is injected into the hot alkali in fine jets and agitated.

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### NEW BOOKS.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492-1892. BY HENRY CARRINGTON BOLTON. (Smithsonian Miscellaneous Collections, Vol. 36.) Octavo, pp. XIII, 1212.

It is not too much to say of this book that one of greater usefulness to the chemist has not appeared within the last twenty-five years. The titles are given under the following heads: I, Bibliography, pp. 1-37; II, Dictionaries and Tables, including Nomenclature, pp. 38-84; III, History of Chemistry, pp. 84-170; IV, Biography, including Bibliographies of Individuals, pp. 171-257; V, Chemistry, Pure and Applied, pp. 258-942; VI, Alchemy, pp. 943-1067; VII, Periodicals, pp. 1068-1164; Addenda and Subject-Index, pp. 1165-1212. Titles in twenty-five languages are catalogued. Of these the titles of German books are most numerous; then come English, French, Latin, Italian, Dutch, Russian, Spanish, and Swedish. The other languages



have less than 100 titles each. Several languages are poorly represented—Finnish, Gujerathi, Hebrew, Hindi, Rumanian, and Welsh have but one each. For most of us, however, this single title will be one too many. The total number of titles indexed is 12,031, of which 273 belong to I, 327 to II, 730 to III, 979 to IV, 8,206 to V, 1,046 to VI, and 470 to VII.

Of Section V, Chemistry, Pure and Applied, Dr. Bolton says : While it "is more extensive than the other six combined, it is the least satisfactory to the editor. Besides pure chemistry it comprises works in every department of chemistry applied to the arts, but not works on the arts themselves; thus agricultural chemistry, but not agriculture; pharmaceutical chemistry, physiological chemistry, etc., find place, but not the sciences of pharmacy and medicine. It is, of course, often impossible to draw the line sharply, and in doubtful cases the tendency has been to include rather than exclude; hence many works on technology are included especially when chemistry lies at their foundation. It is probable, however, that this has not been done uniformly, owing to the difficulty of selection.

"Readers should not expect to find in this section complete lists of the works of a given author; though some pains have been taken in the case of prominent men to catalogue their writings fully (see under Berzelius, Fresenius, Liebig, Johnston, Orfila, Stockhardt, etc). The names of many eminent chemists will be found wanting in Section V, simply because they have published no independent works, although voluminous contributors to periodicals."

The place of publication has been given whenever it could be ascertained but in many cases, perhaps in the majority of cases, not the name of the publisher. In many cases, too, the number of pages is not given—probably it could not be ascertained.

The value of the book is greatly increased by an admirable subject-index.

E. H.

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